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(54) Title: OXIDE LAYER METHOD

(57) Abstract: Methods and apparatus for depositing buffer layers for superconducting articles are provided. Substrate having residual oxide coating is cleaned by interaction with ions, the substrate is resistively heated to a temperature suitable for maintaining acceptable biaxial texture, and buffer material is deposited by sputter-deposition. The deposition methods are suitable for preparing buffer-coated substrates in the form of a tape or wire with lengths substantially in excess of a meter.

Oxide Layer Method

TECHNICAL FIELD

This invention relates to superconductivity, and more particularly to superconducting multi-layered articles and methods of depositing layers for such articles at a high throughput.

BACKGROUND

Coated conductors, comprising a single or multiple combinations of a biaxially textured high temperature superconductor ("HTS") layer on a thin buffer layer and a substrate tape, are a cost-performance-effective technology for manufacturing long length flexible HTS wire for magnet, coil and power applications. For example, these conductors should be useful for power transmission cables, coils of motors and generators, and windings of transformers, as well as for magnets for medical magnetic resonance imaging (MRI), magnetic separation, ion-beam steering and magnetic levitation.

While some background on biaxially textured high temperature superconducting "coated conductors" is known, certain specific challenges in the area of coated conductors such as the need to develop rapid and cost effective methods for depositing effective oxide buffer layers on substrates of practical significance are being investigated.

For example, oxide buffer layers have been deposited for superconductors primarily in a laboratory environment with processes and equipment primarily designed to obtain the appropriate film properties on very short lengths (a few to 10s of cm) without regard to throughput or processing time. Numerous techniques have been tried including evaporation, sputtering, pulsed laser deposition (PLD), sonic jet deposition, and others.

Some of the key elements of the process to obtain epitaxial growth are the vacuum environment, substrate temperature, and deposition rate. Researchers have reported results on short substrate lengths using radio frequency sputtering from metal oxide targets. These typically sputter at undesirably low deposition rates. Reactive

evaporations also have low deposition rates due to reaction of the evaporated species with vacuum environment during the actual deposition. Typical heating approaches have used heated blocks or drums in which the substrate has been in intimate contact during the deposition. This approach can be unreliable in a vacuum environment and also not easily scaleable for coating long lengths of substrate. Further, cleaning of oxides from the substrate surface has been typically carried out by heating in a reducing environment. This can add time and can be incompatible with deposition environments for oxide depositions.

SUMMARY OF THE INVENTION

The invention provides a method of depositing an oxide thin film coating for an epitaxial buffer layer on a substrate by sputtering from a metal target at a high throughput. Heating of the substrate is accomplished by resistive heating or bias and electric potential to obtain an epitaxial morphology. A deposition dwell may be used to form an oxide epitaxial film from a metal target.

In one aspect, the invention provides a method for depositing an epitaxial buffer layer. The method includes exposing the surface of a substrate to ions, such as argon ions (which can be in the form of a beam of accelerated ions, originating from an ion gun, for example, or can be in the form of a plasma) for a time and under conditions sufficient to substantially remove oxides from the surface; heating the substrate; and depositing an epitaxial layer on the substrate surface. The substrate can be in wire or tape form, for example, at least about 1 meter in length. The substrate can be made of ceramaceous materials, metals, metallic alloys (for example, including 5 to 45 atomic percent nickel and balance being copper, which can be biaxially textured), intermetallics, or combinations of these. The substrate can be resistively heated, for example, to a temperature of between 200 and 800°C. The substrate can be substantially continually in motion during the method, by being dispensed from a feeding means and taken up by a recovering means, for example. The deposition of the epitaxial layer can include exposing the surface to metal vapor, which can be generated by magnetron sputtering, originating from a metal target (for example, cerium, nickel, yttrium, ytterbium, gallium, terbium, or palladium targets). Thus, the epitaxial layer can be a metal layer. The method can further include exposing the

surface to oxygen under conditions sufficient to form a metal oxide layer. The method can alternatively or additionally include exposing the surface to nitrogen under conditions sufficient to form a metal nitride layer.

In another aspect, the invention provides another method for depositing an epitaxial buffer layer. The method includes resistively heating the substrate and depositing an epitaxial layer on the substrate surface. The deposition of the epitaxial layer can include exposing the surface to metal vapor, generated by magnetron sputtering, for example. The metal vapor can originate from a metal target (as selected from metals mentioned above). The epitaxial layer can be a metal oxide layer, or a metal nitride layer, for example.

In yet another aspect, the invention provides an apparatus for depositing a material on a substrate. The apparatus includes a vacuum chamber, and the vacuum chamber includes a source of ions for cleaning the surface of the substrate material; a source of current applied to the substrate material (for example, sufficient to resistively heat the substrate material to at least about 200°C, or at least 500°C); and at least one source of metal vapor for depositing metal on the surface of the substrate, where the substrate material is adapted to be sequentially exposed to the source of ions for cleaning, and the source of metal vapor for deposition. The apparatus can further include a source of oxygen for producing metal oxides on the surface of the substrate. The source of current can include at least two current wheels. The source of metal vapor can include at least one magnetron sputter source, which can also include a metal target (nickel, cerium, yttrium, gallium, terbium, ytterbium or palladium). The source of metal vapor can also include at least one vapor stream source, or at least one primer source.

In yet a further aspect, the invention provides another apparatus for depositing a material on a substrate. The apparatus includes a vacuum chamber, the vacuum chamber includes a source of current applied to the substrate material; and at least one source of metal vapor for depositing metal on the surface of the substrate.

In yet a still further aspect, the invention provides a method for depositing an epitaxial buffer layer. The method includes exposing the surface of a substrate to a source of ions for a time and under conditions sufficient to substantially remove oxides from the surface; depositing metal oxides on the substrate surface; and heating the substrate during the exposure and deposition. The deposition of an epitaxial layer on the substrate surface can be carried out substantially normal to the surface. The apparatus can have surfaces and materials positioned so as not to affect the deposition flux. The surfaces can be sufficiently distant from the source of metal vapor and the surface, so that the surfaces do not affect the deposition of metal on the surface.

The invention provides a number of advantages, some of which arise from removing residual metal oxide from a metal substrate surface using a source of energetic ions.

Other advantages may arise from resistively heating the metal substrate during the buffer layer deposition to obtain adequate substrate temperatures during the deposition, or biasing the substrate in a plasma to obtain electron bombardment heating from the plasma to reach appropriate substrate temperatures.

Other advantages may arise from using a sputtering source, for example, in planar or cylindrical configurations, with a metal target to obtain suitable deposition rates. Further advantages arise from the practice of sequentially depositing layers of metal and reacting the metal in an oxygen environment between the depositions of subsequent layers to obtain the proper oxide stoichiometry for each layer.

Further advantages may arise from using substrate guides to pass the substrate surface multiple times before a sputtering source to achieve maximum utilization of the target surface. Further advantages may arise from including payoff and take-up means within a vacuum environment to eliminate the requirement for differential pumping. Further advantages may arise from configuring the deposition chamber so that no surfaces or other materials are able to affect the sputter flux path from a large mean free path normal to the deposition source.

In accordance with the present invention, a high temperature, reducing environment for removing an oxide from the metal substrate prior to epitaxial film

deposition can be eliminated. Reliable and novel methods for heating the tapes are used. Metal targets with magnetron sources are used to deposit oxide buffer layers at relatively high deposition rates. The system geometries lend themselves to high throughputs, and eliminate the complexities of the system and cost for differential pumping.

As used herein, "biaxially textured" refers to a surface for which the crystal grains are in close alignment with a direction in the plane of the surface. One type of biaxially textured surface is a cube-textured surface, in which the crystal grains are also in close alignment with a direction perpendicular to the surface. Examples of cube textured surfaces include the (100)[001] and (100)[011] surfaces, and an example of a biaxially textured surface is the (113)[211] surface. As used herein, "epitaxial layer" refers to a layer of material, the crystallographic orientation of which is directly related to the crystallographic orientation of the surface of a layer of material onto which the epitaxial layer is deposited. For example, for a multi-layer superconductor having an epitaxial layer of superconductor material deposited onto a substrate, the crystallographic orientation of the layer of superconductor material is directly related to the crystallographic orientation of the substrate. If a buffer layer, or layers, is present on the substrate surface, its crystallographic orientation is directly related to that of the substrate, and subsequently deposited superconductor material has crystallographic orientation directly related to that of the buffer layer, or layers. Thus, in addition to the above-discussed properties of a substrate, it can also be desirable for a substrate to have a biaxially textured surface or a cube textured surface.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an illustration of a high temperature superconductor (HTS) coated conductor;

Fig. 2 is an illustration of an alternative embodiment of an HTS coated conductor;

Fig. 3 is an illustration of another alternative embodiment of an HTS coated conductor;

Fig. 4A is an illustration of an apparatus suitable for use in accordance with the present invention;

Fig. 4B is an illustration of an alternative apparatus system suitable for use in accordance with the present invention;

Fig. 4C is an illustration of an alternative apparatus system suitable for use in accordance with the present invention;

Fig. 5 is an illustration of an alternative apparatus system suitable for use in accordance with the present invention;

Fig. 6 is a Θ-2Θ scan for the (200) peak of a CeO_2 film deposited on LAO;

Fig. 7 is a pole figure for a second CeO_2 film deposited on LAO;

Fig. 8 is a Θ-2Θ scan for the (200) peak of a CeO_2 film deposited on a textured nickel strip;

Fig. 9A is a scanning electron micrograph of a CuNiAl substrate before ion cleaning treatment;

Fig. 9B is a scanning electron micrograph of a CuNiAl substrate after ion cleaning treatment;

Fig. 10 is a Θ-2Θ scan for the (200) peak of a Ni primer layer;

Fig. 11 is a Θ-2Θ scan for the (200) peak of a CeO_2 layer sputtered onto a Ni primer layer;

Fig. 12 is a Θ-2Θ scan for the (200) peak of a CeO_2 layer sputtered onto a LAO single crystal; and

Fig. 13 is a Θ-2Θ scan for the (200) peak of a YSZ film sputtered onto a Ni substrate.

DETAILED DESCRIPTION

Referring to Fig. 1, high temperature superconductor (HTS) articles such as 10, particularly in the form of wires or tapes, generally comprise a substrate 12, at least one buffer coating 14, a superconducting layer 16 (formed of, for example, YBCO, or YBCO in which Y has been partially or completely replaced by a rare earth element, or REBCO), and a cap layer 18. The invention provides improved methods of depositing one or more buffer layers on such articles.

Substrates 12 for use in superconductors can be formed by deformation texturing, such as by rolling deformation and annealing, and can subsequently include a layer of oxide on the surface.

The substrate can be formed of alloys having one or more surfaces that are biaxially textured (e.g., (113)[211]) or cube textured (e.g., (100)[001] or (100)[011]). The alloys can have a relatively low Curie temperature (e.g., at most about 80K, at most about 40K, or at most about 20K).

In certain embodiments, the substrate is a binary alloy that contains two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, gold and zinc. For example, a binary alloy can be formed of nickel and chromium (e.g., nickel and at most 20 atomic percent chromium, nickel and from about five to about 18 atomic percent chromium, or nickel and from about 10 to about 15 atomic percent chromium). As another example, a binary alloy can be formed of nickel and copper (e.g., copper and from about five to about 45 atomic percent nickel, copper and from about 10 to about 40 atomic percent nickel, or copper and from about 25 to about 35 atomic percent nickel). A binary alloy can further include relatively small amounts of impurities (e.g., less than about 0.1 atomic percent of impurities, less than about 0.01 atomic percent of impurities, or less than about 0.005 atomic percent of impurities).

In some embodiments, the substrate contains more than two metals (e.g., a ternary alloy or a quarternary alloy). In these embodiments the alloy can contain one or more oxide formers (e.g., Mg, Al, Ti, Cr, Ga, Ge, Zr, Hf, Y, Si, Pr, Eu, Gd, Tb, Dy, Ho, Lu, Th, Er, Tm, Be, Ce, Nd, Sm, Yb and/or La, with Al being the preferred oxide former), as well as two of the following metals: copper, nickel, chromium, vanadium, aluminum, silver, iron, palladium, molybdenum, gold and zinc. The alloys can contain at least about 0.5 atomic percent oxide former (e.g., at least about one atomic percent oxide former, or at least about two atomic percent oxide former) and at most about 25 atomic percent oxide former (e.g., at most about 10 atomic percent oxide former, or at most about four atomic percent oxide former). For example, the alloy can include an oxide former (e.g., at least about 0.5 aluminum), from about 25 atomic percent to about 55 atomic percent nickel (e.g., from about 35 atomic percent to about 55 atomic percent nickel, or from about 40 atomic percent to about 55 atomic percent nickel) with the balance being copper. As another example, the alloy can include an oxide former (e.g., at least about 0.5 atomic aluminum), from about five atomic percent to about 20 atomic percent chromium (e.g., from about 10 atomic percent to about 18 atomic percent chromium, or from about 10 atomic percent to about 15 atomic percent chromium) with the balance being nickel. The alloys can include relatively small amounts of impurities (e.g., less than about 0.1 atomic percent of impurities, less than about 0.01 atomic percent of impurities, or less than about 0.005 atomic percent of impurities).

An alloy can be produced by, for example, combining the constituents in powder form, melting and cooling or, for example, by diffusing the powder constituents together in solid state. The alloy can then be formed by deformation texturing (e.g, annealing and rolling, swaging, extrusion and/or drawing) to form a textured surface (e.g., biaxially textured or cube textured). Alternatively, the alloy constituents can be stacked in a jelly roll configuration, and then deformation textured. In some embodiments, a material with a relatively low coefficient of thermal expansion (e.g, Nb, Mo, Ta, V, Cr, Zr, Pd, Sb, NbTi, an intermetallic such as NiAl or Ni_3Al, or mixtures thereof) can be formed into a rod and embedded into the alloy prior to deformation texturing.

These methods are described in commonly owned U.S. Patent Application No. 09/283,775, filed March 31, 1999, and entitled "Alloy Materials;" commonly owned U.S. Patent Application No. 09/283,777, filed March 31, 1999, and entitled "Alloy Materials;" PCT Publication No. WO 99/17307, published on April 8, 1999, and entitled "Substrates with Improved Oxidation Resistance;" and PCT Publication No. WO 99/16941, published on April 8, 1999, and entitled "Substrates for Superconductors".

The methods involve the use of a substrate that is generally useful for commercial purposes. The substrate is eventually coated with one or more (typically, multiple) layers to form a superconducting article. Such substrates are wires or tapes of a variety of types, including those having cross-sections of cylindrical, rectangular or any other shape. The substrates are generally of a length greater than about 50 m, for example at least about 100 meter long, or at least about 500 meters long. The other dimensions of the final wire or tape are much smaller, for example a rectangular cross-sectioned tape can have a width of about 10 cm or less, for example, about 5 cm or less, or about 1 cm or less. The thickness of a substrate tape can be even smaller, for example, about 20 microns or less, or about 50 micrometers or less (for example, less than about 25 microns).

Upon formation of an appropriately textured, substantially oxide-free substrate surface, deposition of a buffer layer can begin. One or more buffer layers, each including a single metal or oxide layer, can be used. In the case of a substrate material that forms a stable surface oxide layer, the surface oxide layer can be randomly textured and can reemerge during initial oxide buffer layer deposition, thus preventing epitaxial growth of the oxide layer.

In some embodiments, stable oxide formation can be mitigated until a first epitaxial (for example, buffer) layer is on the biaxially textured alloy surface by use of an intermediate layer. Intermediate layers suitable for use in the present invention include those epitaxial metal or alloy layers that do not form surface oxides when exposed to conditions as established by P_{O2} and temperature required for the initial

growth of epitaxial buffer layer films. In addition, the buffer layer acts as a barrier to prevent substrate element(s) from migrating to the surface of the intermediate layer and forming oxides during the initial growth of the epitaxial layer. Absent such an intermediate layer, one or more elements in the substrate would be expected to form thermodynamically stable oxide(s) at the substrate surface which could significantly impede the deposition of epitaxial layers due to, for example, lack of texture in this oxide layer.

In some embodiments, the intermediate layer is transient in nature. "Transient," as used herein, refers to an intermediate layer that is wholly or partly incorporated into or with the biaxially textured substrate following the initial nucleation and growth of the epitaxial film. Even under these circumstances, the intermediate layer and biaxially textured substrate remain distinct until the epitaxial nature of the deposited film has been established. The use of transient intermediate layers may be preferred when the intermediate layer possesses some undesirable property, for example, the intermediate layer is magnetic, such as nickel.

Exemplary intermediate metal layers include nickel, gold, silver, palladium, and alloys thereof. Impurities or alloys may include alloys of nickel and/or copper. Epitaxial films or layers deposited on an intermediate layer can include metal oxides, chalcogenides, halides, and nitrides. In preferred embodiments, the intermediate metal layer does not oxidize under epitaxial film deposition conditions.

Care should be taken that the deposited intermediate layer is not completely incorporated into or does not completely diffuse into the substrate before nucleation and growth of the initial buffer layer structure causes the epitaxial layer to be established. This means that after selecting the metal (or alloy) for proper attributes such as diffusion constant in the substrate alloy, thermodynamic stability against oxidation under practical epitaxial buffer layer growth conditions and lattice matching with the epitaxial layer, the thickness of the deposited metal layer has to be adapted to the epitaxial layer deposition conditions, in particular to temperature.

Deposition of the intermediate metal layer can be done in a vacuum process such as evaporation or sputtering, or by electro-chemical means such as electroplating

(with or without electrodes). These deposited intermediate metal layers may or may not be epitaxial after deposition (depending on substrate temperature during deposition), but epitaxial orientation can subsequently be obtained during a post-deposition heat treatment.

In certain embodiments, solution coating processes can be used for deposition of one or a combination of any of the oxide layers on textured substrates; however, they can be particularly applicable for deposition of the initial (seed) layer on a textured metal substrate. The role of the seed layer is to provide 1) protection of the substrate from oxidation during deposition of the next oxide layer when carried out in an oxidizing atmosphere relative to the substrate (for example, magnetron sputter deposition of yttria-stabilized zirconia from an oxide target); and 2) an epitaxial template for growth of subsequent oxide layers. In order to meet these requirements, the seed layer should grow epitaxially over the entire surface of the metal substrate and be free of any contaminants that may interfere with the deposition of subsequent epitaxial oxide layers.

The formation of oxide buffer layers can be carried out so as to promote wetting of an underlying substrate layer. Additionally, in particular embodiments, the formation of metal oxide layers can be carried out using metal alkoxide precursors (for example, "sol gel" precursors), in which the level of carbon contamination can be greatly reduced over other known processes using metal alkoxide precursors.

If the substrate underlying an oxide layer is insufficiently covered by a precursor solution used to make the oxide layer, then the first oxide layer will not provide the desired protection of the substrate from oxidation during deposition of the subsequent oxide layers when carried out in an oxidizing atmosphere relative to the substrate and will not provide a complete template for the epitaxial growth of subsequent layers. By heating a sol gel precursor film, and thereby allowing the precursor to flow into the substrate grain boundary areas, complete coverage can result. The heating can be relatively low temperature, for example, from about 80°C to about 320°C, for example, from about 100°C to about 300°C, or from about 100°C to about 200°C. Such temperatures can be maintained from about 1 to about 60 minutes, for example, from about 2 to about 45 minutes, or from about 15 to about 45

minutes. The heating step can also be carried out using higher temperatures for a shorter time, for example, a film can be processed within two minutes at a temperature of 300°C.

This heating step can be carried out after, or concurrently with, the drying of excess solvent from the sol gel precursor film. It must be carried out prior to decomposition of the precursor film, however.

The carbon contamination accompanying conventional oxide film preparation in a reducing environment (e.g., 4%H_2-Ar) is believed to be the result of an incomplete removal of the organic components of the precursor film. The presence of carbon-containing contaminants C_xH_y and $C_aH_bO_c$ in or near the oxide layer can be detrimental, since they can alter the epitaxial deposition of subsequent oxide layers. Additionally, it is likely that the trapped carbon-containing contaminants buried in the film can be oxidized during the processing steps for subsequent oxide layers, which can utilize oxidizing atmospheres. The oxidation of the carbon-containing contaminants can result in CO_2 formation, and the subsequent blistering of the film, and possible delamination of the film, or other defects in the composite structure. Thus, it is undesirable to allow carbon-containing contaminants arising from metal alkoxide decomposition to become oxidized only after the oxide layer is formed. Preferably, the carbon-containing contaminants are oxidized (and hence removed from the film structure as CO_2) as the decomposition occurs. Also the presence of carbon-containing species on or near film surfaces can inhibit the epitaxial growth of subsequent oxide layers.

According to particular embodiments, after coating a metal substrate or buffer layer, the precursor solution can be air dried, and then heated in an initial decomposition step. Alternatively, the precursor solution can be directly heated in an initial decomposition step, under an atmosphere that is reducing relative to the metal substrate. Once the oxide layer initially nucleates on the metal substrate in the desired epitaxial orientation, the oxygen level of the process gas is increased, for example, by adding water vapor or oxygen. The nucleation step requires from about 5 minutes to about 30 minutes to take place under typical conditions.

These methods are described in U.S. Patent Application Serial No. _____, filed on even date herewith, and entitled "Enhanced Purity Oxide Layer Formation".

In certain embodiments, an epitaxial buffer layer can be formed using a low vacuum vapor deposition process (e.g., a process performed at a pressure of at least about $1x10^{-3}$ Torr). The process can include forming the epitaxial layer using a relatively high velocity and/or focused gas beam of buffer layer material.

The buffer layer material in the gas beam can have a velocity of greater than about one meter per second (e.g., greater than about 10 meters per second or greater than about 100 meters per second). At least about 50% of the buffer layer material in the beam can be incident on the target surface (e.g., at least about 75% of the buffer layer material in the beam can be incident on the target surface, or at least about 90% of the buffer layer material in the beam can be incident on the target surface).

The method can include placing a target surface (e.g., a substrate surface or a buffer layer surface) in a low vacuum environment, and heating the target surface to a temperature which is greater than the threshold temperature for forming an epitaxial layer of the desired material on the target surface in a high vacuum environment (e.g., less than about $1x10^{-3}$ Torr, such as less than about $1x10^{-4}$ Torr) under otherwise identical conditions. A gas beam containing the buffer layer material and optionally an inert carrier gas is directed at the target surface at a velocity of at least about one meter per second. A conditioning gas is provided in the low vacuum environment. The conditioning gas can be contained in the gas beam, or the conditioning gas can be introduced into the low vacuum environment in a different manner (e.g., leaked into the environment). The conditioning gas can react with species (e.g., contaminants) present at the target surface to remove the species, which can promote the nucleation of the epitaxial buffer layer.

The epitaxial buffer layer can be grown on a target surface using a low vacuum (e.g., at least about $1x10^{-3}$ Torr, at least about 0.1 Torr, or at least about 1 Torr) at a surface temperature below the temperature used to grow the epitaxial layer using physical vapor deposition at a high vacuum (e.g., at most about $1x10^{-4}$ Torr).

The temperature of the target surface can be, for example, from about 25°C to about 800°C (e.g., from about 500°C to about 800°C, or from about 500°C to about 650°C).

The epitaxial layer can be grown at a relatively fast rate, such as, for example, at least about 50 Angstroms per second.

These methods are described in U.S. Patent No. 6,027,564, issued February 22, 2000, and entitled "Low Vacuum Process for Producing Epitaxial Layers;" U.S. Patent No. 6,022, 832, issued February 8, 2000, and entitled "Low Vacuum Process for Producing Superconductor Articles with Epitaxial Layers;" and/or commonly owned U.S. Patent Application No. 09/007,372, filed January 15, 1998, and entitled "Low Vacuum Process for Producing Epitaxial Layers of Semiconductor Material".

In certain embodiments, the underlying layer (e.g., a buffer layer or a different superconductor layer) can be conditioned (e.g., thermally conditioned and/or chemically conditioned) so that the superconductor layer is formed on a conditioned surface. The conditioned surface of the underlying layer can be biaxially textured (e.g., (113)[211]) or cube textured (e.g., (100)[011] or (100)[011]), have peaks in an X-ray diffraction pole figure that have a full width at half maximum of less than about 20° (e.g., less than about 15°, less than about 10°, or from about 5° to about 10°), be smoother than before conditioning as determined by high resolution scanning electron microscopy or atomic force microscopy, have a relatively high density, have a relatively low density of impurities, exhibit enhanced adhesion to other material layers (e.g., a superconductor layer or a buffer layer) and/or exhibit a relatively small rocking curve width as measured by x-ray diffraction.

"Chemical conditioning" as used herein refers to a process which uses one or more chemical species (e.g., gas phase chemical species and/or solution phase chemical species) to affect changes in the surface of a material layer, such as a buffer layer or a superconductor material layer, so that the resulting surface exhibits one or more of the above noted properties.

"Thermal conditioning" as used herein refers to a process which uses elevated temperature with or without chemical conditioning to affect changes in the surface of

a material layer, such as a buffer layer or a superconductor material layer, so that the resulting surface exhibits one or more of the above noted properties. Preferably, thermal conditioning occurs in a controlled environment (e.g., controlled gas pressure, controlled gas environment and/or controlled temperature).

Thermal conditioning can include heating the surface of the underlying layer to a temperature at least about 5°C above the deposition temperature or the crystallization temperature of the underlying layer (e.g., from about 15°C to about 500°C above the deposition temperature or the crystallization temperature of the underlying layer, from about 75°C to about 300°C above the deposition temperature or the crystallization temperature of the underlying layer, or from about 150°C to about 300°C above the deposition temperature or the crystallization temperature of the underlying layer). Examples of such temperatures are from about 500°C to about 1200°C (e.g., from about 800°C to about 1050°C). Thermal conditioning can be performed under a variety of pressure conditions, such as above atmospheric pressure, below atmospheric pressure, or at atmospheric pressure. Thermal conditioning can also be performed using a variety of gas environments (e.g., an oxidizing gas environment, a reducing gas environment, or an inert gas environment).

"Deposition temperature" as used herein refers to the temperature at which the layer being conditioned was deposited.

"Crystallization temperature" as used herein refers to the temperature at which a layer of material (e.g., the underlying layer) takes on a crystalline form.

Chemical conditioning can include vacuum techniques (e.g., reactive ion etching, plasma etching and/or etching with fluorine compounds, such as BF_3 and/or CF_4). Chemical conditioning techniques are disclosed, for example, in Silicon Processing for the VLSI Era, Vol. 1, eds. S. Wolf and R.N. Tanber, pp. 539-574, Lattice Press, Sunset Park, CA, 1986.

Alternatively or additionally, chemical conditioning can involve solution phase techniques, such as disclosed in Metallurgy and Metallurgical Engineering Series, 3d ed., George L. Kehl, McGraw-Hill, 1949. Such techniques can include contacting the surface of the underlying layer with a relatively mild acid solution

(e.g., an acid solution containing less about 10 percent acid, less than about two percent acid, or less than about one percent acid). Examples of mild acid solutions include perchloric acid, nitric acid, hydrofluoric acid, hydrochloric acid, acetic acid and buffered acid solutions. In one embodiment, the mild acid solution is about one percent aqueous nitric acid. In certain embodiments, bromide-containing and/or bromine-containing compositions (e.g., a liquid bromine solution) can be used to condition the surface of a buffer layer or a superconductor layer.

This method can be used to form multiple buffer layers (e.g., two, three, four, or more buffer layers), with one or more of the buffer layers having a conditioned surface.

The method can also be used to form multiple superconductor layers, with one or more of the superconductor layers having a conditioned surface. For example, a superconductor layer can be formed and then thermally and/or chemically conditioned as described above. An additional superconductor layer can then be formed on the conditioned surface of the first superconductor layer. This process can be repeated as many times as desired.

These methods are described in commonly owned U.S. Provisional Patent Application No. 60/166, 140, filed November 18, 1999, and entitled "Multi-Layer Articles and Methods of Making Same," and commonly owned U.S. Patent Application Serial No. _____, filed on even date herewith, and entitled "Multi-layer Articles and Methods of Making Same".

A structure 10' having two buffer layers is shown in Fig. 2 where the substrate 12 is covered with a layer 14a and subsequently a second layer 14b. A cap material 18 can also be added. The multiple layers 14a and 14b can include any combination of layers, such as a metal layer 14a with an oxide layer 14b on top, or an oxide layer 14a with another oxide layer 14b on top. Alternatively, referring to Fig. 3, three buffer layers can be utilized. In this arrangement, structure 10'' includes substrate 12 coated with a metal or oxide layer 14a which in turn is coated with additional metal or oxide layers 14b and 14c before deposition of the superconducting layer 16. Layer 16 can be formed of any material capable of supporting layer 14. For example, layer 16

can be formed of a buffer layer material. Examples of buffer layer materials include metals and metal oxides, such as silver, nickel, TbO_x, GaO_x, CeO_2, yttria-stabilized zirconia (YSZ), Y_2O_3, $LaAlO_3$, $SrTiO_3$, $LaNiO_3$, Gd_2O_3, $LaCuO_3$, $SrRuO_3$, $NdGaO_3$, $NdAlO_3$ and nitrides as known in the art. A buffer material can be prepared using solution phase techniques, including metalorganic deposition, such as disclosed in, for example, S.S. Shoup et al., J. Am. Cer. Soc., vol. 81, 3019; D. Beach et al., Mat. Res. Soc. Symp. Proc., vol. 495, 263 (1988); M. Paranthaman et al., Superconductor Sci. Tech., vol. 12, 319 (1999); D.J. Lee et al., Japanese J. Appl. Phys., vol. 38, L178 (1999) and M.W. Rupich et al., I.E.E.E. Trans. on Appl. Supercon. vol. 9, 1527.

A cap material 18 can also be added. Any of the embodiments can further include a cap layer 18. Cap layer 18 can be formed of one or more layers, and preferably includes at least one noble metal layer. "Noble metal," as used herein, is a metal, the reaction products of which are thermodynamically unstable under the reaction conditions employed to prepare the HTS tape. Exemplary noble metals include, for example, silver, gold, palladium, and platinum. Noble metals provide a low interfacial resistance between the HTS layer and the cap layer. In addition, cap layer 18 can include a second layer of normal metal (for example, copper or aluminum or alloys of normal metals.

The overall buffer layer (14a, 14b and 14c) can have a total thickness of from about 0.1 to about 1.0 micrometers, and preferably from about 0.1 to 0.5 micrometers, or more preferably from about 0.1 to 0.2 micrometers.

In some embodiments, a first buffer layer can be formed using ion beam assisted deposition (IBAD). In this technique, a buffer layer material is evaporated using, for example, electron beam evaporation, sputtering deposition, or pulsed laser deposition while an ion beam (e.g., an argon ion beam) is directed at a smooth amorphous surface of a substrate onto which the evaporated buffer layer material is deposited.

For example, the buffer layer can be formed by ion beam assisted deposition by evaporating a buffer layer material having a rock-salt like structure (e.g., a material having a rock salt structure, such as an oxide, including MgO, or a nitride) onto a

smooth, amorphous surface (e.g., a surface having a root mean square roughness of less than about 100 Angstroms) of a substrate so that the buffer layer material has a surface with substantial alignment (e.g., about 13° or less), both in-plane and out-of-plane.

The conditions used during deposition of the buffer layer material can include, for example, a substrate temperature of from about 0°C to about 400°C (e.g., from about room temperature to about 400°C), a deposition rate of from about 1.0 Angstrom per second to about 4.4 Angstroms per second, an ion energy of from about 200 eV to about 1200 eV, and/or an ion flux of from about 110 microamperes per square centimeter to about 120 microamperes per square centimeter.

In some embodiments, the substrate is formed of a material having a polycrystalline, non-amorphous base structure (e.g., a metal alloy, such as a nickel alloy) with a smooth amorphous surface formed of a different material (e.g., Si_3N_4).

In certain embodiments, a plurality of buffer layers can be deposited by epitaxial growth on an original IBAD surface. Each buffer layer can have substantial alignment (e.g., about 13° or less), both in-plane and out-of-plane.

These methods are described in PCT Publication No. WO 99/25908, published on May 27, 1999, and entitled "Thin Films Having A Rock-Salt-Like Structure Deposited on Amorphous Surfaces".

In some preferred embodiments, the substrate is allowed to pass through an apparatus adapted to carry out steps of the deposition method described herein. For example, if the substrate is in the form of a wire or tape, the substrate can be passed linearly from a payout reel to a take-up reel, and steps can be performed on the substrate as it passes between the reels. An apparatus suitable for use with the invention is shown in Fig. 4A. Referring to Fig. 4A, apparatus 20 is shown, including payoff reel 22, first current or voltage source 24, ion gun 26, first sputter source 28, second sputter source 30, guide 32, second current or voltage source 34, take up reel 36 and substrate 38. Substrate proceeds from payoff reel 22, and is subsequently exposed to ion gun 26 and the two sputter sources, 28 and 30. The substrate is resistively heated by application of current or voltage from sources 28 and 34.

Deposition elements 60, 61 and 62 can be further sputter sources, primer sources or vapor stream sources. In particular embodiments, further sputter sources are preferred.

Substrate materials are heated to elevated temperatures which are less than about 90% of the melting point of the substrate material but greater than the threshold temperature for forming an epitaxial layer of the desired material on the substrate material in a vacuum environment at the predetermined deposition rate. In order to form the appropriate or matching buffer layer crystal structure and film buffer layer smoothness, high substrate temperatures are generally preferred. Typical lower limit temperatures for the growth of oxide layers on metal are approximately 200°C to 800°C, preferably 500°C to 800°C, and more preferably, 650°C to 800°C. Various well-known methods such as radiative heating, convection heating, and conduction heating are suitable for short (2 cm to 10 cm) lengths of substrate, but for longer (1m to 100 m) lengths, these techniques may not be well suited. Also to obtain desired high throughput rates in a manufacturing process, the substrate wire or tape must be moving or transferring between deposition stations during the process. The substrates are heated by resistive heating, that is, by passing a current through the metal substrate, which is easily scaleable to long length manufacturing processes. This approach works well while instantaneously allowing for rapid travel between these zones. Temperature control can be accomplished by using optical pyrometers and closed loop feedback systems to control the power supplied to the substrate being heated. Current can be supplied to the substrate by electrodes that contact the substrate in at least two different segments of the substrate. For example, if the substrate, in the form of a tape or wire, is passed between reels, the reels themselves could act as electrodes. Alternatively, if guides are employed to transfer the substrate between reels, the guides could act as electrodes. The electrodes could also be completely independent of any guides or reels as well. In some preferred embodiments, current is applied to the tape between current wheels.

Deposition of buffer layers is performed in a vacuum chamber, and is achieved by sputtering, typically Ar^+ (argon sputtering). During a deposition, the chamber is first evacuated of air, and then a low-pressure amount of sputtering gas

(for example, argon) is admitted into the chamber. Sputtering metal-oxide buffer layers from metal oxide targets includes an rf-sputtering approach to eliminate charging and arcing of the cathode-target assembly during the deposition. This method results in stoichiometric or nearly stoichiometric oxide buffer layers. However, this method also results in very low deposition rate since oxide targets have very low sputter efficiencies (one to two orders in magnitude less than metals), and attempting to apply high power levels to ceramic or oxide targets leads to non-uniform heating of the oxide target and subsequent cracking and destruction of the target. In a preferred embodiment, by sputtering of a metal target to initially grow a metal film on the substrate and then after the substrate passes the deposition zone dwelling in an environment that is appropriately oxidizing, the appropriate oxide stoichiometry can be obtained. This preferred embodiment can be used to obtain higher deposition rates, higher manufacturing throughput, and also reduce capital costs. Metal oxide films may also be grown without using the oxidizing environment dwell by providing a process gas atmosphere that is oxidizing relative to the metal being deposited but reducing relative to the substrate surface. Electrically conductive materials such as Al, W, Ce, and Ti can use a d.c. power source, in which the target acts as the cathode in a diode system.

Sputter sources can be categorized as dc and rf diode, dc and rf triode, and planar and cylindrical magnetron sources which can be used with rf, dc, or pulsating dc. The magnetron sources enhance the sputtering efficiency by a more effective ionization process by utilizing magnets behind the source. Simply speaking the magnetic field created by permanent or electromagnets trap ionized particles near the face of the target thus significantly confining the ionization process for the Ar ions. This results in higher deposition rates. In a preferred embodiment, magnetron sources are used to increase deposition rates, which increases coating throughput and reduces manufacturing costs. This magnetic field configuration confines the electrons in a region close to the cathode surface. These confined electrons add to the ionization of the inert gas and significantly increase the sputtering rate of the cathode material. High deposition rates can be achieved with this process.

Deposition of a buffer layer is carried out until a desired coating thickness is achieved. The desired coating thickness will be determined by the functionality of the buffer layer and monitored or controlled by either deposition time or in-line rate monitors.

Exemplary metals that can be used as targets in direct current sputtering techniques include, for example, nickel, cerium, yttrium, gallium, terbium, ytterbium, and palladium. The metals are desirably at least about 99% pure, more desirably at least about 99.9% pure and most desirably at least about 99.99% pure, as measured by inductively coupled plasma or similar known methods.

The metal target, acting as an anode, is able to assume a variety of shapes and configurations according to the geometry of the sputtering apparatus. For example, the anode can be a planar target or a cylindrical target.

An alternative apparatus system for use in the invention is shown in Fig. 4B. In the embodiment, provision is made for the use of a primer, or intermediate, layer on the substrate. Referring to Fig. 4B, apparatus 70 is shown, including payoff reel 22, first current or voltage source 24, ion gun 26, primer source 40, first sputter source 28, guide 32, second current or voltage source 34, take up reel 36 and substrate 38. Substrate proceeds from payoff reel 22, and is subsequently exposed to ion gun 26, the primer source 40, and the sputter source 30. The substrate is resistively heated by application of current or voltage from sources 24 and 34. Deposition elements 60, 61 and 62 can be further sputter sources.

An alternative apparatus system for use in the invention is shown in Fig. 4C. In the embodiment, provision is made for the use of a vapor stream source. Referring to Fig. 4C, apparatus 50 is shown, including payoff reel 22, first current or voltage source 24, ion gun 26, primer source 40, vapor stream source 42, guide 32, second current or voltage source 34, take up reel 36 and substrate 38. Substrate proceeds from payoff reel 22, and is subsequently exposed to ion gun 26, primer source 40 and vapor stream source 42. Alternatively, primer source 40 in Fig. 4C can be a vapor stream source. That is, generally a substrate can be exposed to an ion gun, followed optionally by exposure to a primer source, followed by exposure to either

sputter sources or vapor stream sources. As previously mentioned, the substrate is resistively heated by application of current or voltage from sources 24 and 34. Deposition elements 60, 61 and 62 can be further vapor stream sources.

A further alternative apparatus system for use in the invention is shown in Fig. 5. In the embodiment, the vapor stream is deposited onto the tape in a direction normal to the tape surface. Referring to Fig. 5, apparatus 80 is shown, including payoff reel 22, first current or voltage source 24, sputter source 61, second current or voltage source 34, third current or voltage source 35, second sputter source 62, fourth current or voltage source 64, and take up reel 36. Substrate 38 travels from payoff reel 22 to take up reel 36. The entire apparatus is surrounded by chamber walls 7, 9, 11 and 13. Arrows 66 and 68 represent flux that emanates from first deposition element 61 and second deposition element 62. As substrate 38 passes before the deposition sources, material is deposited on the heated substrate 38 only between first and second current or voltage sources 24 and 34, and between third and fourth current or voltage sources 35 and 64. The substrate 38 is only at proper deposition temperature between these wheels. As the substrate contacts the current wheels, the substrate cools because the wheels are efficient heat sinks. Thus, the sputter flux 66 and 68 should be deposited substantially normal to the substrate surface. Thus, the sputter flux 66 or 68 should be confined and deposited on the substrate 38 in the region only at the proper deposition temperature between these wheels. This can be facilitated by making a large distance between any physical elements other than the substrate, such as chamber wall 9 and sputter source 62, or between chamber wall 11 and sputter source 61. By placing the chamber walls and any other surfaces or objects at a significant normal distance from the corresponding sputter sources, the sputter flux and energy diffuse and decay in a line of sight manner into the space, rather than, otherwise, being deflected and possibly deposited on substrate 38 in a region not at the proper deposition temperature.

In certain embodiments, a precursor solution is formed of an organic solution containing metal trifluoroacetates prepared from powders of $BaCO_3$, $YCO_3 \cdot 3H_2O$ and $Cu(OH)_2CO_3$ combined and reacted using methods known to those skilled in the art. For example, the powders can be combined in a 2:1:3 ratio with between 20-30%

(5.5-6.0 M) excess trifluoroacetic acid in methyl alcohol and then refluxed (e.g., for approximately four to ten hours) to produce a solution substantially 0.94 M based on copper content.

The precursor solution is then applied to a surface (e.g., a buffer layer surface), such as by spin coating or other techniques known to those skilled in the art.

After application to the surface (e.g, the buffer layer surface), the precursor solution is heat treated. Generally, the solution is heated at a rate of from about 0.5°C per minute to about 10°C per minute in moist oxygen (e.g., having a dew point in the range of from about 20°C to about 75°C) to a temperature in the range of from about 300°C to about 500°C. The coating is then heated for about one hour to a temperature of less than about 860°C (e.g., less than about 810°C) in a moist reducing nitrogen-oxygen gas mixture (e.g., having a composition including from about 0.5% to about 5% oxygen). Optionally, the coating can be further heated to a temperature of from about 860°C to about 950°C for from about five to about 25 minutes. The coating is subsequently heated to a temperature of from about 400°C to about 500°C for at least about eight hours at in dry oxygen. The coating can then be cooled to room temperature in static dry oxygen.

These methods are described in U.S. Patent No. 5,231,074, issued on July 27, 1993, and entitled "Preparation of Highly Textured Oxide Superconducting Films from MOD Precursor Solutions".

In some embodiments, a metal oxyfluoride is deposited using one or more standard techniques, such as metalorganic solution deposition, metalorganic chemical vapor deposition, reactive evaporation, plasma spray, molecular beam epitaxy, laser ablation, ion beam sputtering, electron beam evaporation, depositing a metal trifluoroacetate coating and decomposing the coating as described herein. Multiple layers of metal oxyfluoride may be deposited.

Other constituent metallic elements of the desired oxide superconductor are also deposited in substantially stoichiometric proportions.

The metal oxyfluoride is converted into an oxide superconductor at a rate of conversion selected by adjusting temperature, vapor pressure of gaseous water or

both. For example, the metal oxyfluoride can be converted in a processing gas having a moisture content of less than 100% relative humidity (e.g., less than about 95% relative humidity, less than about 50% relative humidity, or less than about 3% relative humidity) at 25°C to form some oxide superconductor, then completing the conversion using a processing gas having a higher moisture content (e.g., from about 95% relative humidity to about 100% relative humidity at 25°C). The temperature for converting the metal oxyfluoride can be in the range of from about 700°C to about 900°C (e.g., from about 700°C to about 835°C). The processing gas preferably contains from about 1 volume percent oxygen gas to about 10 volume percent oxygen gas.

These methods are described in PCT Publication No. WO 98/58415, published on December 23, 1998, and entitled "Controlled Conversion of Metal Oxyfluorides into Superconducting Oxides".

In certain embodiments, the superconductor layer can be formed from a precursor composition that has a relatively small amount of free acid. In aqueous solutions, this can correspond to a precursor composition with a relatively neutral pH (e.g., neither strongly acidic nor strongly basic). The precursor composition can be used to prepare multi-layer superconductors using a wide variety of materials which can be used as the underlying layer on which the superconductor layer is formed.

The total free acid concentration of the precursor composition can be less than about $1x10^{-3}$ molar (e.g., less than about $1x10^{-5}$ molar or about $1x10^{-7}$ molar). Examples of free acids that can be contained in a precursor composition include trifluoroacetic acid, acetic acid, nitric acid, sulfuric acid, acids of iodides, acids of bromides and acids of sulfates.

When the precursor composition contains water, the precursor composition can have a pH of at least about 3 (e.g., at least about 5 or about 7).

In some embodiments, the precursor composition can have a relatively low water content (e.g., less than about 50 volume percent water, less than about 35 volume percent water, less than about 25 volume percent water).

In embodiments in which the precursor composition contains trifluoroacetic acid and an alkaline earth metal (e.g., barium), the total amount of trifluoroacetic acid can be selected so that the mole ratio of fluorine contained in the precursor composition (e.g., in the form of trifluoroacetate) to the alkaline earth metal (e.g., barium ions) contained in the precursor composition is at least about 2:1 (e.g., from about 2:1 to about 18.5:1, or from about 2:1 to about 10:1).

Superconducting articles formed from such precursor compositions can include more than one superconductor layer (e.g., two superconductor layers disposed on each other). The combined thickness of the superconductor layers can be at least about one micron (e.g., at least about two microns, at least about three microns, at least about four microns, at least about five microns, or at least about six microns). The combined critical current density of the superconductor layers can be at least about $5x10^5$ Amperes per square centimeter (e.g., at least about $1x10^6$ Amperes per square centimeter, or at least about $2x10^6$ Amperes per square centimeter).

In general, the precursor compositions can be prepared by combining soluble compounds of a first metal (e.g., copper), a second metal (e.g., an alkaline earth metal), and a rare earth metal with one or more desired solvents and optionally water. As used herein, "soluble compounds" of the first, second and rare earth metals refer to compounds of these metals that are capable of dissolving in the solvent(s) contained in the precursor compositions. Such compounds include, for example, salts (e.g., nitrates, acetates, alkoxides, iodides, sulfates and trifluoroacetates), oxides and hydroxides of these metals.

These methods and compositions are described in commonly owned U.S. Provisional Patent Application Serial No. 60/166, 297, filed on November 18, 1999, and entitled "Superconductor Articles and Compositions and Methods for Making Same," and commonly owned U.S. Patent Application No. _____, filed on even date herewith, and entitled "Superconductor Articles and Compositions and Methods for Making Same".

In certain embodiments, the preparation of the superconductor layer includes using a precursor composition containing a trifluoroacetate salt of one or more metals

and a controlled total water content (e.g., controlled content of liquid water in the precursor composition and controlled content of water vapor in the surrounding environment) present when treating the precursor composition to form an intermediate of the superconductor layer (e.g., a metal oxyfluoride intermediate of the superconductor layer). For example, the precursor composition can have a relatively low water content (e.g., less than about 50 volume percent water, less than about 35 volume percent water, or less than about 25 volume percent water) and/or a relatively high solids content, whereas the surrounding gas environment can have a relatively high vapor pressure of water (e.g., from about 5 Torr to about 50 Torr water, from about 5 Torr to about 30 Torr water, or from about 10 Torr to about 25 Torr water). The superconductor layer intermediate (e.g., metal oxyfluoride intermediate) can be formed in a relatively short period of time (e.g., less than about five hours, less than about three hours, or less than about one hour).

Treating the precursor composition can include heating the precursor composition from an initial temperature (e.g., room temperature) to a temperature of from about 190°C to about 215°C (e.g., about 210°C) at a rate of at least about 5°C per minute (e.g., at least about 8°C per minute, or at least about 10°C per minute) in a water vapor pressure of from about 5 Torr to about 50 Torr water vapor (e.g., from about 5 Torr to about 30 Torr water vapor, or from about 10 Torr to about 25 Torr water vapor) . The nominal partial pressure of oxygen can be, for example, from about 0.1 Torr to about 760 Torr.

Heating is then continued to a temperature of from about 220°C to about 290°C (e.g., about 220°C) at a rate of from about 0.05°C per minute to about 0.4°C per minute (e.g., from about 0.1°C per minute to about 0.4°C per minute) in a water vapor pressure of from about 5 Torr to about 50 Torr water vapor (e.g., from about 5 Torr to about 30 Torr water vapor, or from about 10 Torr to about 25 Torr water vapor). The nominal partial pressure of oxygen can be, for example, from about 0.1 Torr to about 760 Torr.

This is followed by heating to about 400°C at a rate of at least about 2°C per minute (e.g., at least about 3°C per minute, or at least about 5°C per minute) in a water vapor pressure of from about 5 Torr to about 50 Torr water vapor (e.g., from

about 5 Torr to about 30 Torr water vapor, or from about 10 Torr to about 25 Torr water vapor) to form an intermediate of the superconductor material (e.g., a metal oxyfluoride intermediate). The nominal partial pressure of oxygen can be, for exampie, from about 0.1 Torr to about 760 Torr.

The intermediate can be heated to form the desired superconductor layer. For example, the intermediate can be heated to a temperature of from about 700°C to about 825°C in an environment containing from about 0.1 Torr to about 50 Torr oxygen and from about 0.1 Torr to about 150 Torr water vapor (e.g., about 12 Torr water vapor) with the balance being, for example, nitrogen and/or argon.

The method can result in a well-ordered superconductor layer (e.g., biaxially textured or cube textured) having a relatively high critical current density (e.g., at least about $5x10^5$ Amperes per square centimeter).

These methods are described in commonly owned U.S. Provisional Patent Application Serial No. 60/166,145, filed on November 18, 1999, and entitled "Methods and Compositions for Making a Multi-Layer Article," and commonly owned U.S. Patent Application No. _____, filed on even date herewith, and entitled "Methods and Compositions for Making a Multi-layer Article".

In certain embodiments, the superconducting layer can be formed from solid-state, or semi solid state, precursor materials deposited in the form of a dispersion. These precursor compositions allow for example the substantial elimination of $BaCO_3$ formation in final YBCO superconducting layers, while also allowing control of film nucleation and growth.

Two general approaches are presented for the formulation of precursor compositions. In one approach, the cationic constituents of the precursor composition are provided in components taking on a solid form, either as elements, or preferably, compounded with other elements. The precursor composition is provided in the form of ultrafine particles which are dispersed so that they can be coated onto and adhere onto the surface of a suitable substrate, intermediate-coated substrate, or buffer-coated substrate. These ultrafine particles can be created by aerosol spray, by evaporation or by similar techniques which can be controlled to provide the chemical compositions

and sizes desired. The ultrafine particles are less than about 500 nm, preferably less than about 250 nm, more preferably less than about 100 nm and even more preferably less than about 50 nm. In general, the particles are less than about 50% the thickness of the desired final film thickness, preferably less than about 30% most preferably less than about 10% of the thickness of the desired final film thickness. For example, the precursor composition can comprise ultrafine particles of one or more of the constituents of the superconducting layer in a substantially stoichiometric mixture, present in a carrier. This carrier comprises a solvent, a plasticizer, a binder, a dispersant, or a similar system known in the art, to form a dispersion of such particles. Each ultrafine particle can contain a substantially compositionally uniform, homogeneous mixture of such constituents. For example, each particle can contain BaF_2, and rare-earth oxide, and copper oxide or rare earth/barium/copper oxyfluoride in a substantially stoichiometric mixture. Analysis of such particles would desirably reveal a rare-earth:barium:copper ratio as substantially 1:2:3 in stoichiometry, with a fluorine:barium ratio of substantially 2:1 in stoichiometry. These particles can be either crystalline, or amorphous in form.

In a second approach, the precursor components can be prepared from elemental sources, or from a substantially stoichiometric compound comprising the desired constituents. For example, evaporation of a solid comprising a substantially stoichiometric compound of desired REBCO constituents (for example, $YBa_2Cu_3O_{6.8}$) or a number of solids, each containing a particular constituent of the desired final superconducting layer (for example, Y_2O_3, BaF_2, CuO) could be used to produce the ultrafine particles for production of the precursor compositions. Alternatively, spray drying or aerosolization of a metalorganic solution comprising a substantially stoichiometric mixture of desired REBCO constituents could be used to produce the ultrafine particles used in the precursor compositions. Alternatively, one or more of the cationic constituents can be provided in the precursor composition as a metalorganic salt or metalorganic compound, and can be present in solution. The metalorganic solution can act as a solvent, or carrier, for the other solid-state elements or compounds. According to this embodiment, dispersants and/or binders can be substantially eliminated from the precursor composition. For example, the precursor

composition can comprise ultrafine particles of rare-earth oxide and copper oxide in substantially a 1:3 stoichiometric ratio, along with a solublized barium-containing salt, for example, barium-trifluoroacetate dissolved in an organic solvent, such as methanol.

If the superconducting layer is of the REBCO type, the precursor composition can contain a rare earth element, barium, and copper in the form of their oxides; halides such as fluorides, chlorides, bromides and iodides; carboxylates and alcoholates, for example, acetates, including trihaloacetates such as trifluroracetates, formates, oxalates, lactates, oxyfluorides, propylates, citrates, and acetylacetonates, and, chlorates and nitrates. The precursor composition can include any combination of such elements (rare earth element, barium, and copper) in their various forms, which can convert to an intermediate containing a barium halide, plus rare earth oxyfluoride and copper(oxyfluoride) without a separate decomposition step or with a decomposition step that is substantially shorter than that which may be required for precursors in which all constituents are solubilized, and without substantial formation of $BaCO_3$, and which can subsequently be treated using high temperature reaction processes to yield an epitaxial REBCO film with T_c of no less than about 89K, and J_c greater than about 500,000 A/cm^2 at a film thickness of 1 micron or greater. For example, for a $YBa_2Cu_3O_{6.8}$ superconducting layer, the precursor composition could contain barium halide (for example, barium fluoride), yttrium oxide (for example, Y_2O_3), and copper oxide; or yttrium oxide, barium trifluoroacetate in a trifluoroacetate/methanol solution, and a mixture of copper oxide and copper trifluoroacetate in trifluoroacetate/methanol. Alternatively, the precursor composition could contain Ba-trifluoroacetate, Y_2O_3, and CuO. Alternatively, the precursor composition could contain barium trifluoroacetate and yttrium trifluoroacetate in methanol, and CuO. Alternatively, the precursor composition could contain BaF_2 and yttrium acetate and CuO. In some preferred embodiments, barium-containing particles are present as BaF_2 particles, or barium fluoroacetate. In some embodiments the precursor could be substantially a solublized metalorganic salt containing some or all of the cation constituents, provided at least a portion of one of the compounds

containing cation constituents present in solid form. In certain embodiments, the precursor in a dispersion includes a binder and/or a dispersant and/or solvent(s).

The precursor compositions can be applied to substrate or buffer-treated substrates by a number of methods, which are designed to produce coatings of substantially homogeneous thickness. For example, the precursor compositions can be applied using spin coating, slot coating, gravure coating, dip coating, tape casting, or spraying. The substrate is desirably uniformly coated to yield a superconducting film of from about 1 to 10 microns, preferably from about 1 to 5 microns, more preferably from about 2 to 4 microns.

More details are provided in commonly owned United States Patent Application Serial No. 09/500,717, filed on February 9, 2000, and entitled "Coated Conductor Thick Film Precursor".

In particular embodiments, methods can be employed to minimize the formation of undesirable a-axis oriented oxide layer grains, by inhibiting the formation of the oxide layer until the required reaction conditions are attained.

Conventional processes developed for decomposition and reaction of fluoride-containing precursors use a constant, and low, non-turbulent flow of process gas that is introduced into the decomposition furnace in an orientation that is parallel to the film surface, resulting in a stable boundary layer at the film/gas interface. In the apparatus types typically used for oxide layer precursor decomposition and reaction, the diffusion of gaseous reactants and products through this gas/film boundary layer appears to control the overall reaction rates. In thin, small area films (for example, less than about 0.4 microns thick and less than about a square centimeter), the diffusion of H_2O into the film and the diffusion of HF out of the film occur at rates such that the formation of the $YBa_2Cu_3O_{7-x}$ phase does not begin at any significant rate until the sample reaches the processing temperature. However, as the film thickness or area increases, the rates of gaseous diffusion into and out of the film decrease, all other parameters being equal. This results in longer reaction times and/or incomplete formation of the $YBa_2Cu_3O_{7-x}$ phase, resulting in reduced crystallographic texture, lower density, and reduced critical current density. Thus, the

overall rate of $YBa_2Cu_3O_{7-x}$ phase formation is determined, to a significant extent, by the diffusion of gases through the boundary layer at the film surface.

One approach to eliminating these boundary layers is to produce a turbulent flow at the film surface. Under such conditions, the local gas composition at the interface is maintained essentially the same as in the bulk gas (that is, the pH_2O is constant, and the pHF is approximately zero). Thus, the concentration of the gaseous products/reactants in the film is not controlled by the diffusion through the gas/film surface boundary layer condition, but rather by diffusion through the film. In order to minimize the nucleation of a-axis $YBa_2Cu_3O_{7-x}$ oriented grains on a substrate surface, the formation of the $YBa_2Cu_3O_{7-x}$ phase is inhibited until desired process conditions are reached. For example, the formation of the $YBa_2Cu_3O_{7-x}$ phase can be inhibited until desired process temperature is reached.

In one embodiment, a combination of: 1) low (non-turbulent) process gas flow, so that a stable boundary layer is established at the film/gas interface, during the ramp to temperature, and 2) high (turbulent) process gas flow, so that the boundary layer is disrupted at the film/gas interface, is employed. For example, in a three inch tube furnace, the flow can be from about 0.5 to about 2.0 L/min during the temperature ramp from ambient temperature to the desired process temperature. Thereafter, the flow can be increased to a value of from about 4 to about 15 L/min during the time at which the film is being processed. Thus, the rate of formation of $YBa_2Cu_3O_{7-x}$ and epitaxial texture formation can be increased at high temperature, while minimizing the amount of unwanted a-axis nucleation and growth at low temperature during ramp up. According to these processes, a-axis nucleated grains are desirably present in an amount of less than about 1%, as determined by scanning electron microscopy.

More details are provided in commonly owned U.S. Patent Application Serial No. _____, filed on even date herewith, and entitled "Control of Oxide Layer Reaction Rates".

In certain embodiments, a metal oxyfluoride intermediate of a superconductor material can be prepared using a process that involves relatively few temperature ramps (e.g., less than three ramps, such as two ramps).

Alternatively or additionally, forming the metal oxyfluoride can include one or more steps in which the temperature is held substantially constant (e.g., constant within about 10°C, within about 5°C, within about 2°C, within about 1°C) for a relatively long period of time (e.g., more than about one minute, more than about five minutes, more than about 30 minutes, more than about an hour, more than about two hours, more than about four hours) after a first temperature ramp to a temperature greater than about room temperature (e.g., at least about 50°C, at least about 100°C, at least about 200°C, at least about 215°C, from about 215°C to about 225°C, about 220°C).

Formation of the metal oxyfluoride intermediate can involve using more than one gas environment (e.g., a gas environment having a relatively high water vapor pressure and a gas environment having a relatively low water vapor pressure) while maintaining the temperature substantially constant (e.g., constant within about 10°C, within about 5°C, within about 2°C, within about 1°C) for a relatively long period of time (e.g., more than about one minute, more than about five minutes, more than about 30 minutes, more than about an hour, more than about two hours, more than about four hours). As an example, in a high water vapor pressure environment, the water vapor pressure can be from about 5 Torr to about 40 Torr (e.g., from about 25 Torr to about 38 Torr, such as about 32 Torr). A low water vapor pressure environment can have a water vapor pressure of less than about 1 Torr (e.g., less than about 0.1 Torr, less than about 10 milliTorr, about five milliTorr).

Generally, the metal oxyfluoride is formed by disposing a composition (e.g., a precursor solution) on a surface (e.g., a substrate surface, a buffer layer surface or a superconductor layer surface) and heating the composition. The methods of disposing the composition on the surface include spin coating, dip coating, web coating and other techniques known in the art.

Typically, in an initial decomposition step, the initial temperature in this step is about room temperature, and the final temperature is from about 215□C to about 225°C using a temperature ramp of 10□C per minute or less. During this step, the partial pressure of water vapor in the nominal gas environment is preferably maintained at from about 5 Torr to about 40 Torr. The partial pressure of oxygen in the nominal gas environment can be maintained at from about 0.1 Torr to about 760 Torr. The temperature and nominal gas environment are then held substantially constant for a relatively long period of time.

After this time period, the gas environment is changed to a relatively dry gas environment (e.g., less than about one Torr water vapor, less than about 0.1 Torr water vapor, less than about 10 milliTorr water vapor, five milliTorr water vapor) while maintaining the temperature substantially constant. The temperature and nominal gas environment are then held substantially constant for a relatively long period of time.

After this time period, the nominal gas environment is maintained substantially constant and heating is continued to a temperature sufficient to form the metal oxyfluoride intermediate (e.g., about 400□C). This step is preferably performed using a temperature ramp of 10□C per minute or less.

The metal oxyfluoride intermediate can then be heated to form the desired superconductor layer. Typically, this step is performed by heating to a temperature of from about 700□C to about 825□C. During this step, the nominal gas environment typically can contain from about 0.1 Torr to about 50 Torr oxygen and from about 0.1 Torr to about 150 Torr (e.g., about 12 Torr) of water vapor with the balance being nitrogen and/or argon. Preferably, the metal oxyfluoride intermediate has a relatively low defect density.

These methods are described in commonly owned U.S. Patent Application Serial No. _____, filed on even date herewith, and entitled "Methods of Making A Superconductor".

Other alternative configurations are suitable for the inventive methods.

In some embodiments, multi-layer high temperature superconductors are provided, including first and second high temperature superconductor coated elements. Each element includes a substrate, at least one buffer layer deposited on the substrate, a high temperature superconductor layer, and a cap layer. The first and second high temperature superconductor coated elements are joined at the first and second cap layers. Exemplary joining techniques include soldering and diffusion bonding.

Such a multi-layer architecture provides improved current sharing, lower hysteretic losses under alternating current conditions, enhanced electrical and thermal stability, and improved mechanical properties. Useful conductors can be made having multiple tapes stacked relative to one another and/or laminated to provide sufficient ampacity, dimensional stability, and mechanical strength. Such embodiments also provide a means for splicing coated tape segments and for termination of coated tape stackups or conductor elements.

Moreover, it is expected that this architecture can provide significant benefits for alternating current applications. AC losses are shown to be inversely proportional to the effective critical current density within the conductor, more specifically, the cross-sectional area within which the current is carried. For a multifilimentary conductor, this would be the area of the "bundle" of superconducting filaments, excluding any sheath material around that bundle. For a "face-to-face" architecture, the "bundle" critical current density would encompass only the high temperature superconductor films and the thickness of the cap layer structure. The cap layer can be formed of one or more layers, and preferably includes at least one noble metal layer. "Noble metal," as used herein, is a metal, the reaction products of which are thermodynamically unstable under the reaction conditions employed to prepare the HTS tape. Exemplary noble metals include, for example, silver, gold, palladium, and platinum. Noble metals provide a low interfacial resistance between the HTS layer and the cap layer. In addition, the cap layer can include a second layer of normal metal (for example, copper or aluminum or alloys of normal metals). In direct current applications, additional face-to-face wires would be bundled or stacked to provide for the required ampacity and geometry for a given application.

Additionally, the high temperature superconductor film on the surface of the tapes could be treated to produce local breaks, that is, non-superconducting regions or stripes in the film only along the length of the tape (in the current flow direction). The cap layer deposited on the high temperature superconductor film would then serve to bridge the nonsuperconducting zones with a ductile normal metal region. An offset in the edge justification of the narrow strips or filaments, similar to a running bond brick pattern, would allow current to transfer to several narrow superconducting filaments both across the cap layers and to adjacent filaments, further increasing the redundancy and improving stability.

In all embodiments, a normal metal layer could be included along the edge of the conductor to hermetically seal the high temperature superconductor films and to provide for current transfer into the film, and if necessary, from the film into the substrate.

In particular embodiments, tensile strain on the superconducting layers can be minimized by providing the superconducting layer within a neutral mechanical axis zone. A "neutral mechanical axis" of a flexible material in the form of a tape of layered materials is a plane in the plane of the tape, coplanar with the layers of the tape, in which tensile strain experienced upon bending the material in a direction normal to the plane is zero. An operational layer centered on this axis will experience minimum tensile strain. A "neutral mechanical axis zone" is a region where the maximum strain experienced by the superconducting layer is less than that which would lead to degraded performance. The criterion for positioning the operational layer within the neutral mechanical axis zone is derived by balancing the moments in bending. This is done by properly specifying the thicknesses, positions, and Young's modulus of the laminate layer or layers; laminate layers are those layers which are non-operational, and can include substrate, buffer and cap layers, for example.

More details are provided in commonly owned U.S. Provisional Patent Application Serial No. 60/145,458, filed on July 23, 1999, and entitled "Enhanced High Temperature Coated Superconductors," and commonly owned United States Patent Application Serial No. _____, filed concurrently herewith, and entitled "Enhanced High Temperature Coated Superconductors".

In some embodiments, coated conductors can be fabricated in a way that minimizes losses incurred in alternating current applications. The conductors are fabricated with multiple conducting paths, each of which comprises path segments which extend across at least two conducting layers, and further extend between these layers.

Each superconducting layer has a plurality of conductive path segments extending across the width of the layer, from one edge to another, and the path segments also have a component of direction along the length of the superconducting layer. The path segments in the superconducting layer surface are in electrically conductive communication with interlayer connections, which serve to allow current to flow from one superconducting layer to another. Paths, which are made up of path segments, are periodically designed, so that current flow generally alternates between two superconducting layers in bilayered embodiments, and traverses the layers through interlayer connections.

Superconducting layers can be constructed to contain a plurality of path segments which extend both across their widths and along their lengths. For example, superconducting layers can be patterned so as to achieve a high resistivity or a fully insulating barrier between each of the plurality of path segments. For example, a regular periodic array of diagonal path segments can be imposed on the layer along the full length of the tape. Patterning of superconducting layers to give such arrays can be accomplished by a variety of means known to those skilled in the art, including for example, laser scribing, mechanical cutting, implantation, localized chemical treatment through a mask, and other known methods. Further, the superconducting layers are adapted to allow the conductive path segments in their surfaces to electrically communicate with conducting interlayer connections passing between the layers, at or near their edges. The interlayer connections will typically be normally conducting (not superconducting) but in special configurations could also be superconducting. Interlayer connections provide electrical communication between superconducting layers which are separated by non-conducting or highly resistive material which is positioned between the superconducting layers. Such non-

conducting or highly resistive material can be deposited on one superconducting layer. Passages can be fabricated at the edges of the insulating material to allow the introduction of interlayer connections, followed by deposition of a further superconducting layer. One can achieve a transposed configuration with coated conductors by patterning a superconducting layer into filaments parallel to the axis of the tape and winding the tape in a helical fashion around a cylindrical form.

More details are provided in commonly owned United States Patent Application Serial No. 09/500,718, filed on February 9, 2000, and entitled "Coated Conductors with Reduced AC Loss."

The invention will be further described in the following examples, which do not limit the scope of the invention described in the claims.

EXAMPLES

We have demonstrated certain key process elements to obtain the appropriate epitaxial properties by using a sputter technique with a metal target and by diffusing oxygen into the film during a deposition dwell to obtain an epitaxial film.

Example 1: Magnetron Sputtered CeO_2 from Metal Target on Single Crystal LAO

A cerium oxide film was sputtered at a substrate temperature of 600°C to 700°C on a single crystal LAO substrate using a cerium metal target and magnetron source. The appropriate (CeO_2) stoichiometry was obtained by diffusing oxygen into the film during a deposition dwell. Epitaxial growth, judged by the CeO_2 (200) peak, was obtained as noted in Fig. 6 from the Θ-2Θ scans and pole figures for a second deposition, shown in Fig. 7.

Example 2: Magnetron Sputtered CeO_2 from Metal Target on Textured Nickel Strip

A cerium oxide film was sputtered at a substrate temperature of 600°C to 700°C on a textured Ni strip using a cerium metal target and magnetron source.

The appropriate (CeO_2) stoichiometry was obtained by diffusing oxygen into the film during a deposition dwell. Epitaxial growth, judged by the CeO_2 (200) peak, was obtained as noted in Fig. 8 from the Θ-2Θ scans.

Example 3: Ion Beam Etching of Non-magnetic Alloy Substrates

A CuNiAl substrate was cleaned using ion cleaning techniques to remove a randomly oriented film of Al_2O_3 and Al_2O_3 nodules which prevent the epitaxial growth of quality oriented buffer layers on non-magnetic substrates to form YBCO superconductors. Figs. 9A and 9B are high resolution scanning electron micrographs (100k x), showing the alloy substrate surface before (Fig. 9A) and after (Fig. 9B) the ion cleaning treatment, noting the removal of the oxide film and nodules.

Example 4: Ion Beam Etching Followed by Epitaxial Primer and CeO_2 Seed Layers on Non-magnetic Alloy Substrates

A 5mm wide x 10 mm long sample of biaxially textured alloy substrate was ion-etched at 1000 eV to remove the 20-30 nm thick native oxide. The sample was then coated with a 200 nm thick layer of Ni by sputtering at a chamber pressure of 125 mT and power level or 200W. The Ni primer layer was biaxially textured as shown by the Θ-2Θ scans in Fig. 10. Subsequently, 20-30 nm thick epitaxial layer of CeO_2 was deposited using magnetron sputtering from a metal target using a substrate temperature between 600°C and 700°C, with Θ-2Θ scans shown in Fig. 11.

Example 5: High Temperature Buffer Layer Deposition on Single Crystal Substrates Heated Using Current Wheels

A YSZ single crystal substrate was attached to a 2m long Inconnel strip using a high thermal conductivity paste. Current was passed through the strip, heating the substrate to 650°C to 800°C. Temperature was monitored and controlled with an optical pyrometer. A cerium oxide film was sputtered on an LAO single

crystal substrate using a magnetron source. Epitaxial growth, judged by the CeO_2 (200) peak, was obtained as noted in Fig. 12, from the Θ-2Θ scans.

Example 6: High Temperature Buffer Layer Deposition on Metal Substrates Heated Using Current Wheels

A 10mm wide x 50 mm long sample of biaxially textured Ni substrate was coated with an epitaxial seed layer of 20 nmk of CeO_2. The sample was spliced into a longer length of Ni, which was approximately 2-3 m ion length. This length of Ni was heated to 700°C to 800°C using current wheels and coated while transferring past a yttria-stabilized zirconia (YSZ) magnetron target. The coating thickness was 200-300 nm thick. Fig. 13 is a Θ-2Θ scan and shows the 200 texture of the YSZ film.

OTHER EMBODIMENTS

It is to be understood that while the invention has been described in conjunction with the detailed description thereof, the foregoing description is intended to illustrate and not limit the scope of the invention, which is defined by the scope of the appended claims. Other aspects, advantages, and modifications are within the scope of the following claims.

What is claimed is:

1. A method for depositing an epitaxial buffer layer, the method comprising:

exposing the surface of a substrate to ions for a time and under conditions sufficient to substantially remove oxides from the surface;

heating the substrate; and

depositing an epitaxial layer on the substrate surface.

2. The method of claim 1, wherein the ions to which the substrate surface is exposed are in the form of a beam of accelerated ions.

3. The method of claim 2, wherein the ions originate from an ion gun.

4. The method of claim 1, wherein the ions to which the substrate surface is exposed are in the form of a plasma.

5. The method of claim 1, wherein the ions are argon ions.

6. The method of claim 1, wherein the substrate has a form selected from the group consisting of wire and tape.

7. The method of claim 6, wherein the tape is at least about 1 meter in length.

8. The method of claim 1, wherein the substrate is a material selected from the group consisting of ceramaceous materials, metals, metallic alloys, intermetallics, and combinations thereof.

9. The method of claim 8, wherein the substrate is a metallic alloy.

10. The method of claim 9, wherein the alloy comprises 5 to 45 atomic percent nickel and balance being copper.

11. The method of claim 8, wherein the substrate is biaxially textured.

12. The method of claim 1, wherein the substrate is resistively heated.

13. The method of claim 12, wherein the substrate is resistively heated to a temperature of between 200 and 800°C.

14. The method of claim 13, wherein the substrate is substantially continually in motion during the method.

15. The method of claim 14, wherein the substrate is dispensed from a feeding means and taken up by a recovering means.

16. The method of claim 1, wherein the deposition of the epitaxial layer comprises exposing the surface to metal vapor.

17. The method of claim 16, wherein the metal vapor is generated by magnetron sputtering.

18. The method of claim 16, wherein the metal vapor originates from a metal target.

19. The method of claim 19, wherein the metal target is selected from the group consisting of cerium, nickel, yttrium, ytterbium, gallium, terbium, and palladium targets.

20. The method of claim 16, wherein the epitaxial layer is a metal layer.

21. The method of claim 16, further comprising exposing the surface to oxygen under conditions sufficient to form a metal oxide layer.

22. The method of claim 16, further comprising exposing the surface to nitrogen under conditions sufficient to form a metal nitride layer.

23. A method for depositing an epitaxial buffer layer, the method comprising resistively heating the substrate and depositing an epitaxial layer on the substrate surface.

24. The method of claim 23, wherein the deposition of the epitaxial layer comprises exposing the surface to metal vapor.

25. The method of claim 24, wherein the metal vapor is generated by magnetron sputtering.

26. The method of claim 25, wherein the metal vapor is originates from a metal target.

27. The method of claim 26, wherein the metal target is selected from the group consisting of cerium, nickel, yttrium, ytterbium, gallium, terbium, and palladium targets.

28. The method of claim 24, wherein the epitaxial layer is a metal layer.

29. The method of claim 24, wherein the epitaxial layer is a metal oxide layer.

30. The method of claim 24, wherein the epitaxial layer is a metal nitride layer.

31. An apparatus for depositing a material on a substrate, the apparatus comprising a vacuum chamber, the vacuum chamber comprising:

a source of ions for cleaning the surface of the substrate material;

a source of current applied to the substrate material; and

at least one source of metal vapor for depositing metal on the surface of the substrate, wherein the substrate material is adapted to be sequentially exposed to the source of ions for cleaning, and the source of metal vapor for deposition.

32. The apparatus of claim 31, further comprising a source of oxygen for producing metal oxides on the surface of the substrate.

33. The apparatus of claim 31, wherein the source of current is sufficient to resistively heat the substrate material to at least about 200°C.

34. The apparatus of claim 33, wherein the source of current is sufficient to resistively heat the substrate material to at least about 500°C.

35. The apparatus of claim 31, wherein the source of current comprises at least two current wheels.

36. The apparatus of claim 31, wherein the source of metal vapor comprises at least one magnetron sputter source.

37. The apparatus of claim 36, wherein the magnetron sputter source further comprises a metal target.

38. The apparatus of claim 37, wherein the metal target comprises nickel, cerium, yttrium, gallium, terbium, ytterbium or palladium.

39. The apparatus of claim 31, wherein the source of metal vapor comprises at least one vapor stream source.

40. The apparatus of claim 31, further comprising at least one primer source.

41. An apparatus for depositing a material on a substrate, the apparatus comprising a vacuum chamber, the vacuum chamber comprising:

a source of current applied to the substrate material; and

at least one source of metal vapor for depositing metal on the surface of the substrate.

42. A method for depositing an epitaxial buffer layer, the method comprising:

exposing the surface of a substrate to a source of ions for a time and under conditions sufficient to substantially remove oxides from the surface;

depositing metal oxides on the substrate surface; and

heating the substrate during the exposure and deposition. The method of claim 1, wherein the deposition of an epitaxial layer on the substrate surface is substantially normal to the surface.

43. The apparatus of claim 41, wherein surfaces and materials are positioned so as not to affect the deposition flux.

44. The method of claim 42, wherein the deposition of metal oxides on the substrate surface is substantially normal to the surface.

45. The apparatus of claim 31, wherein surfaces are sufficiently distant from the source of metal vapor and the surface, so that the surfaces do not affect the deposition of metal on the surface.

46. The method of claim 44, wherein the surfaces and materials are charged.

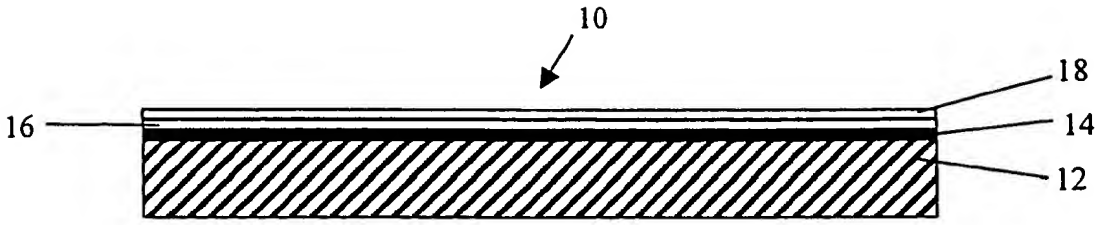


Fig. 1

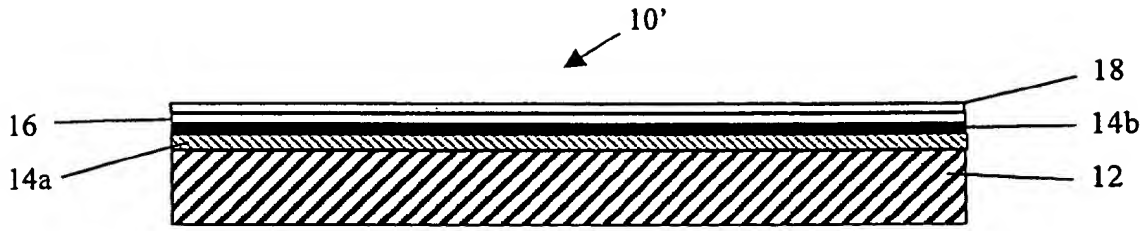
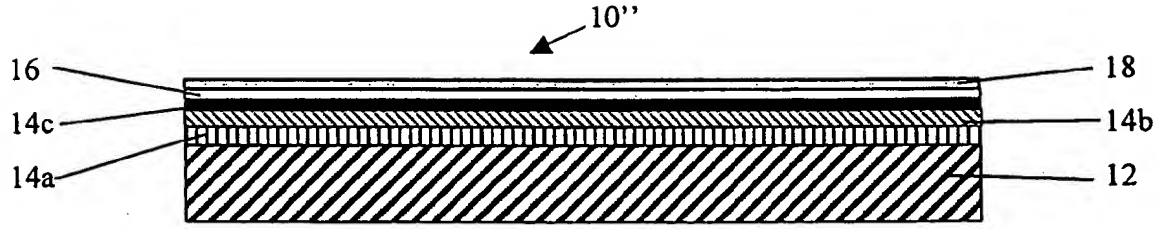


Fig. 2



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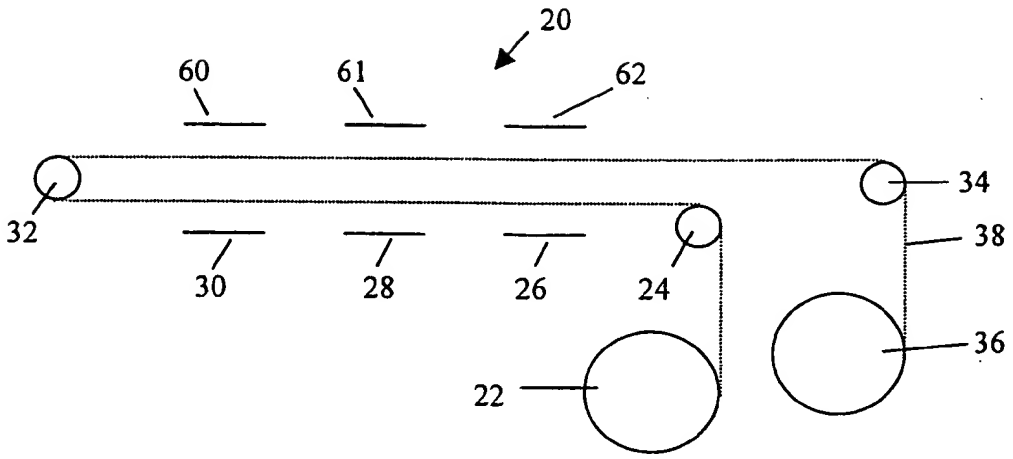
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Fig. 4A

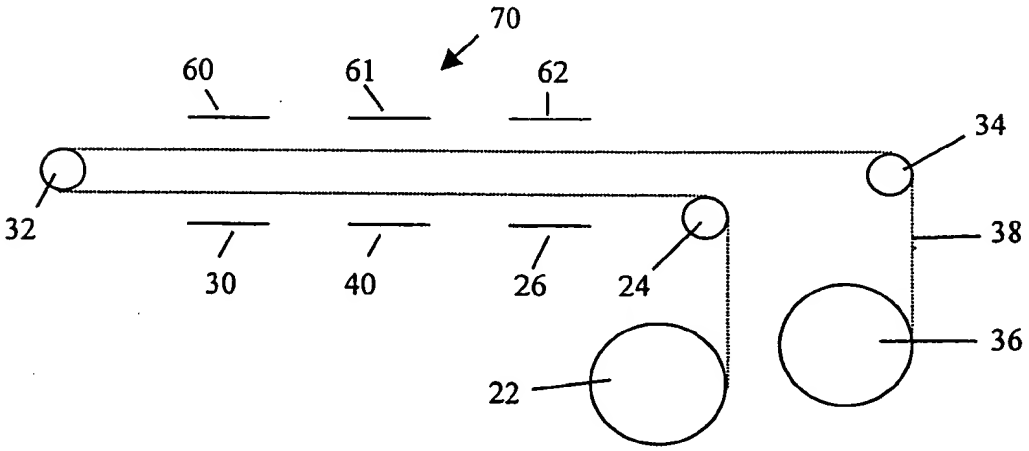
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Fig. 4B

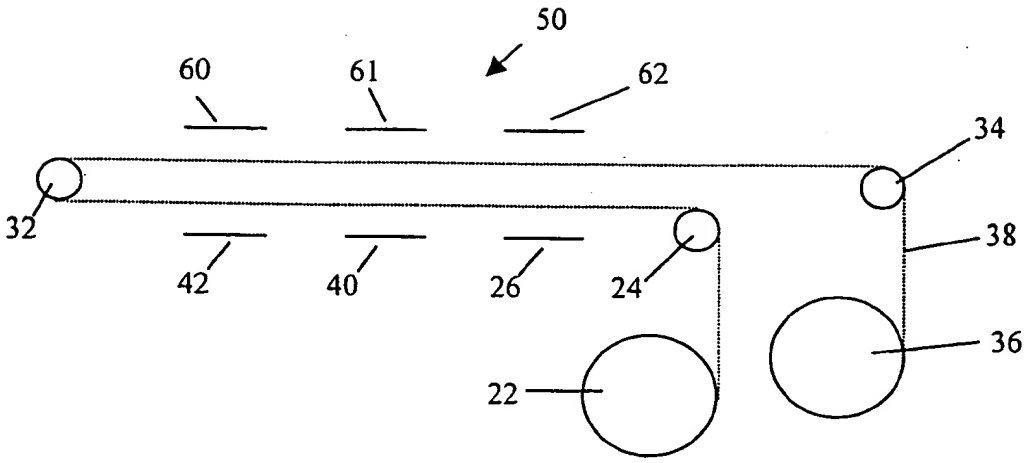
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Fig. 4C

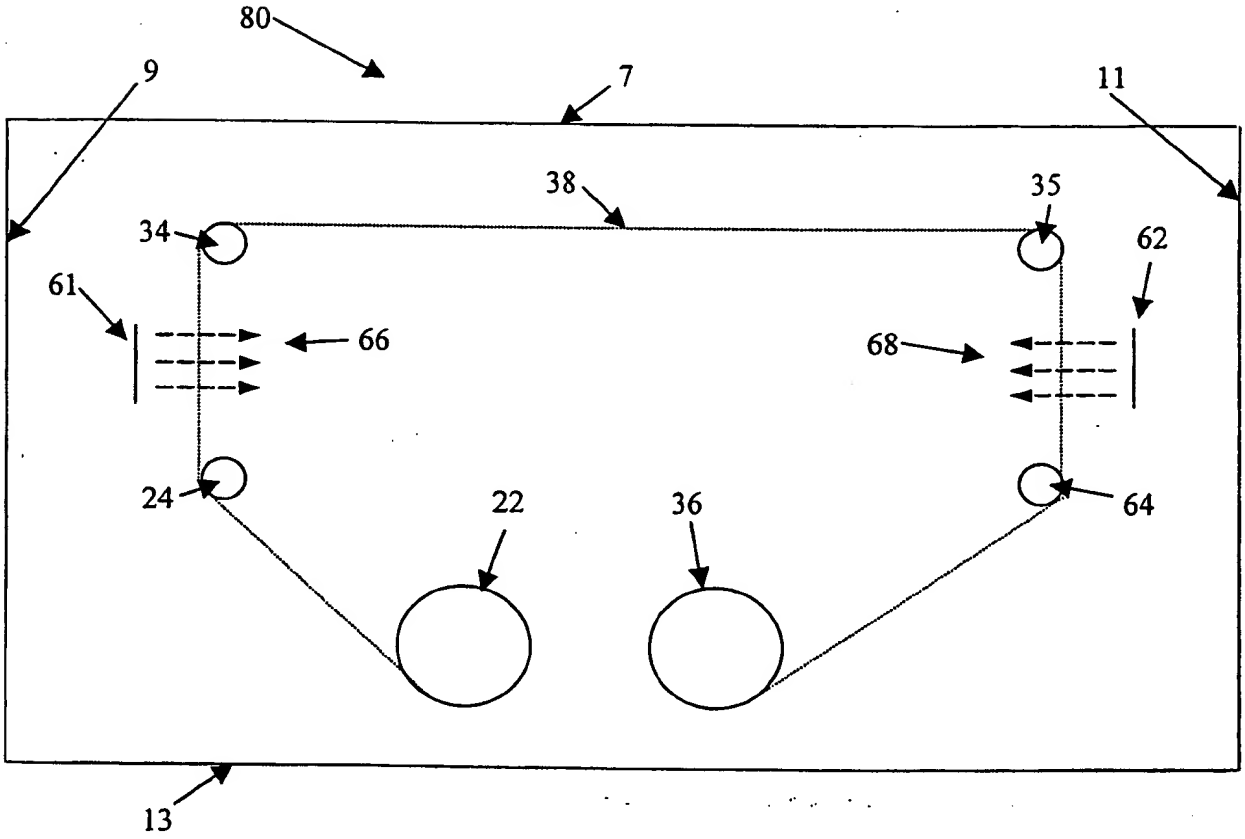
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Fig. 5

Fig 6

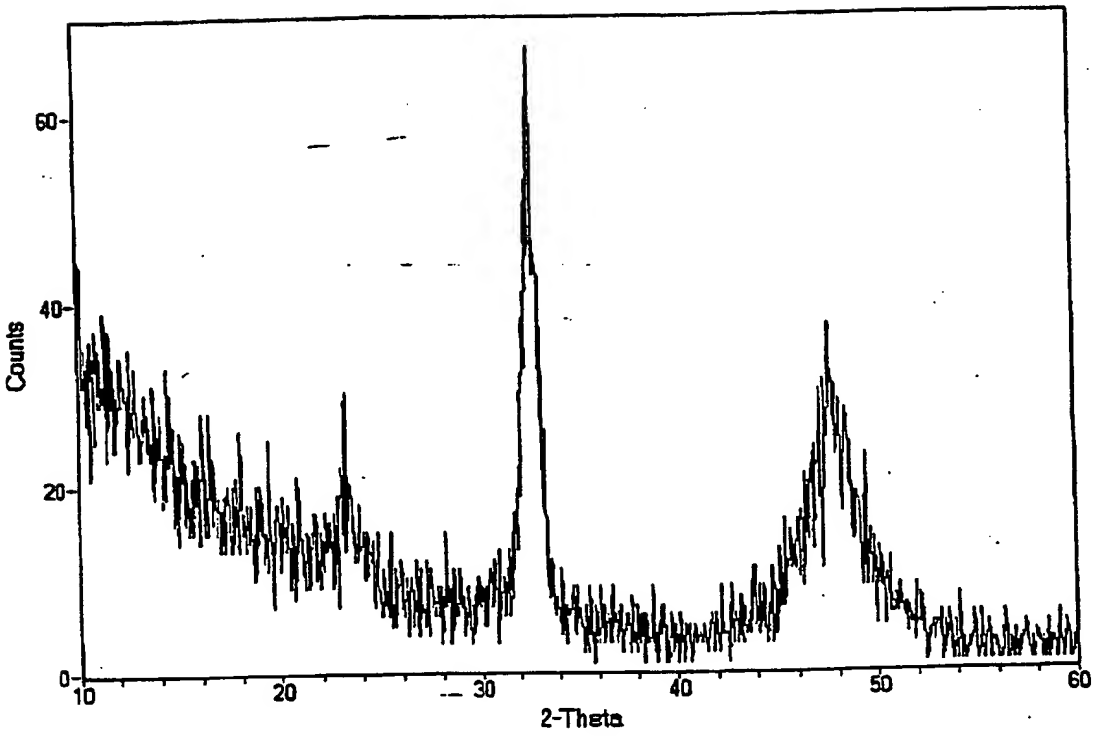
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Fig 7.

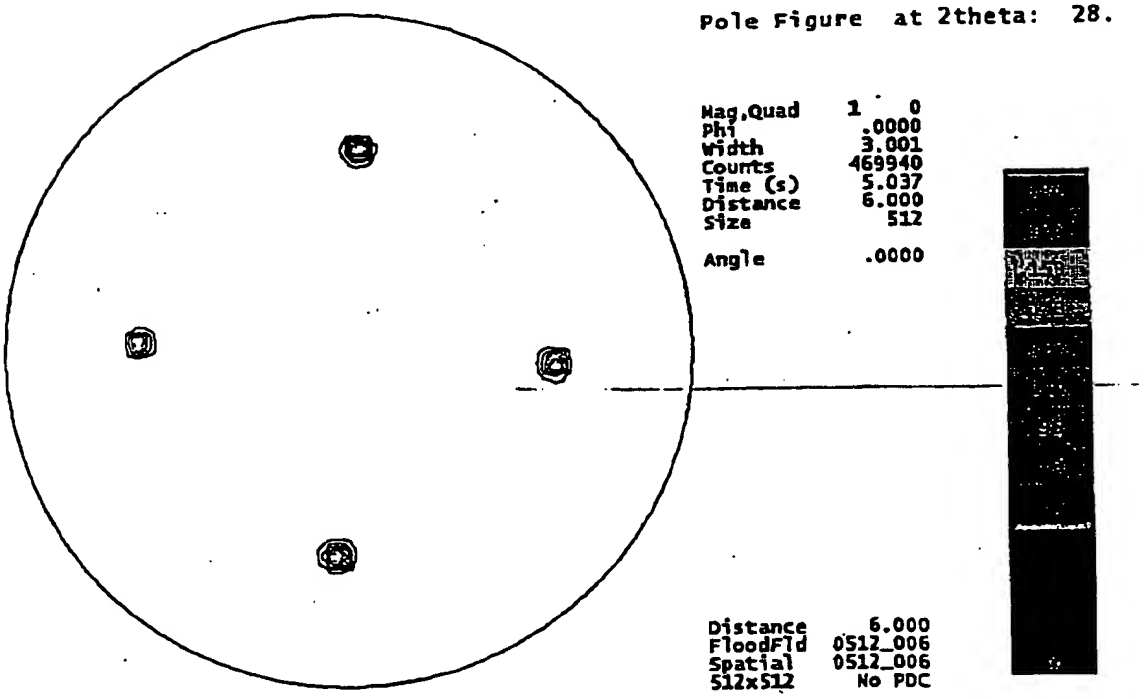
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Fig 8.

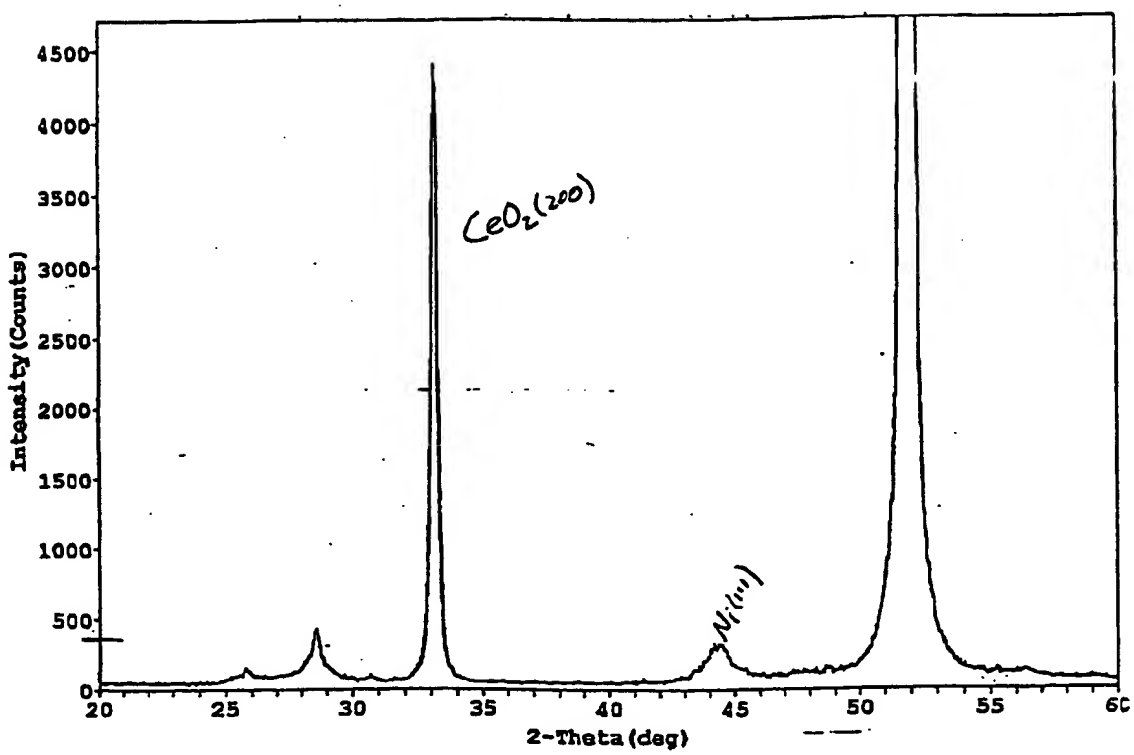


Fig 9A

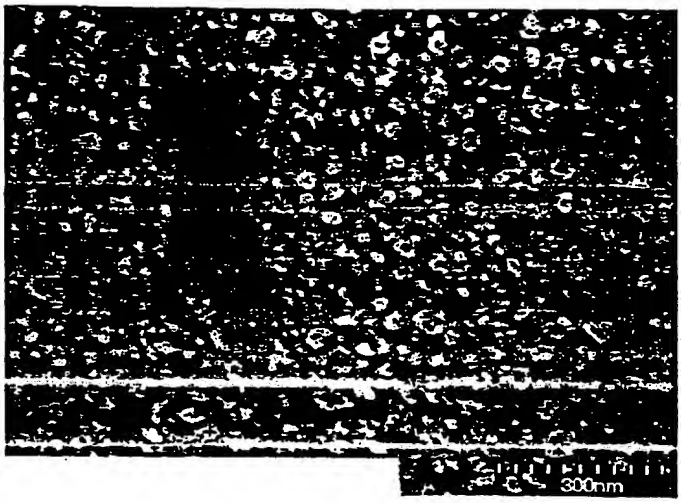


Fig 9B

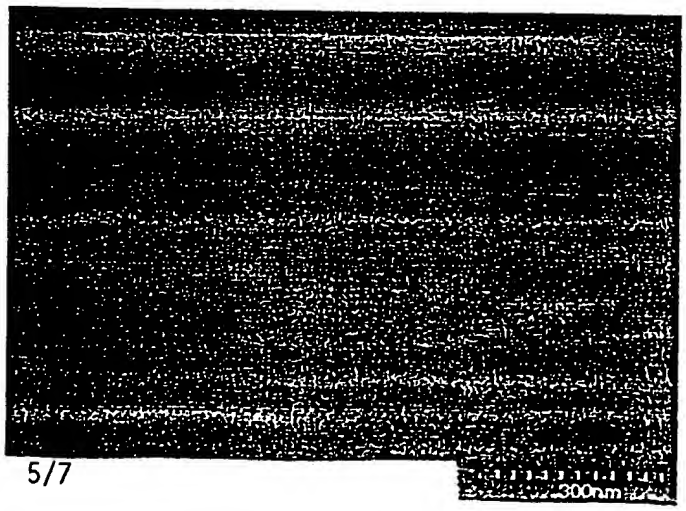
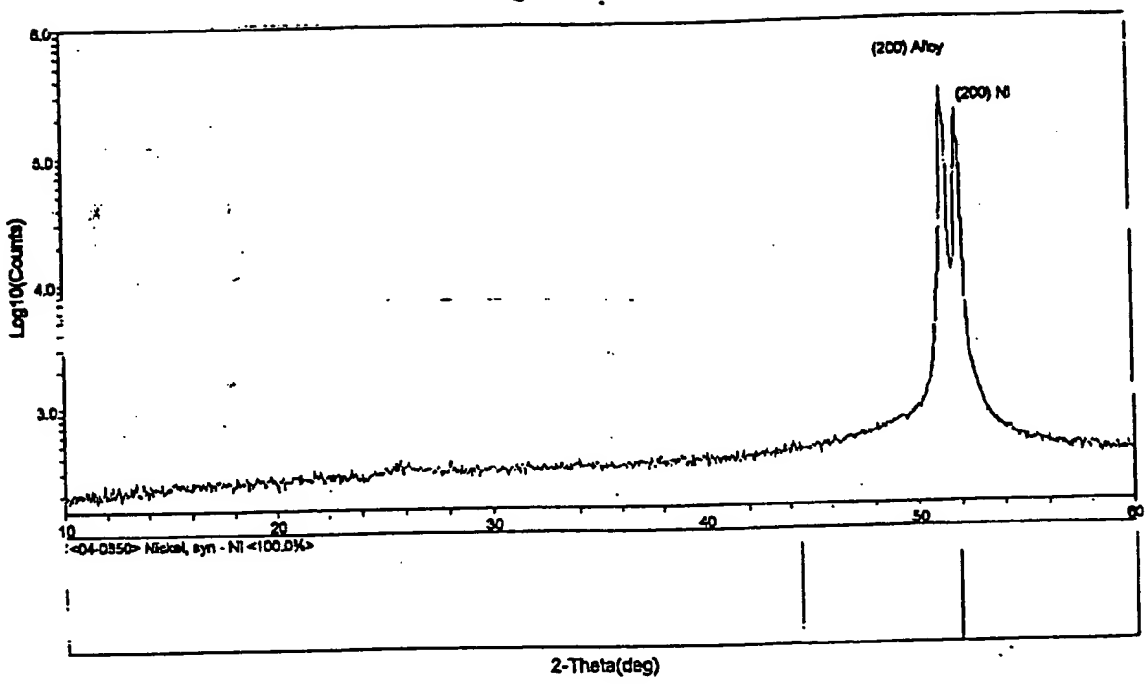


Fig. 10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(200) Ni
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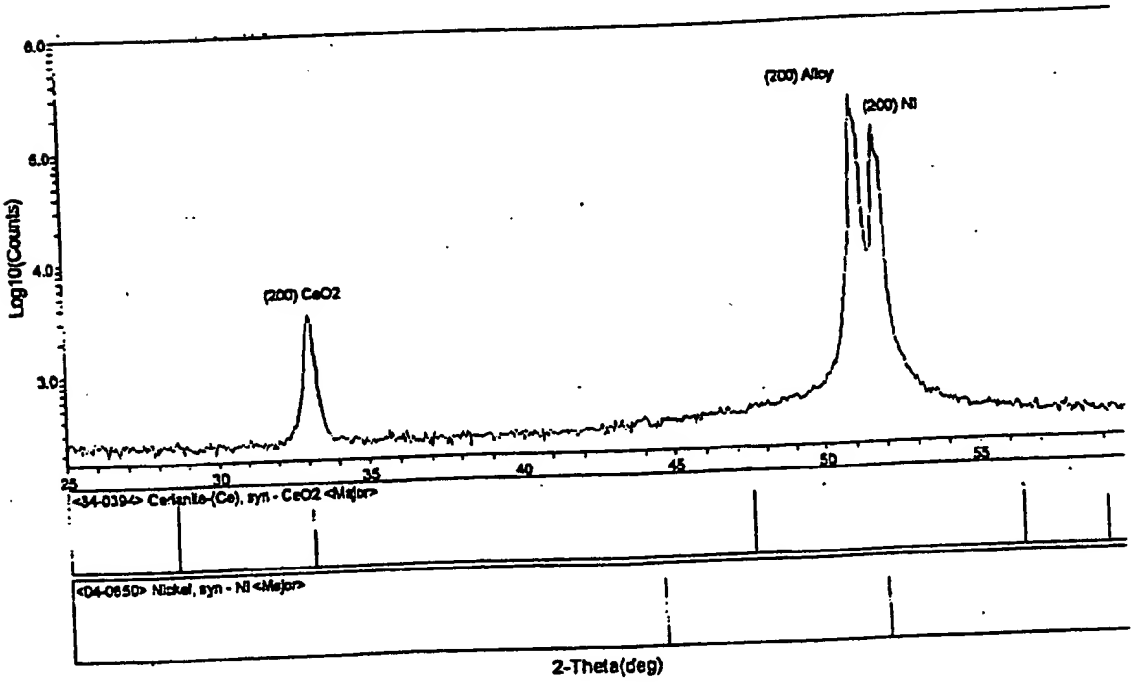
Fig. 11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2-Theta(deg)

Fig. 12

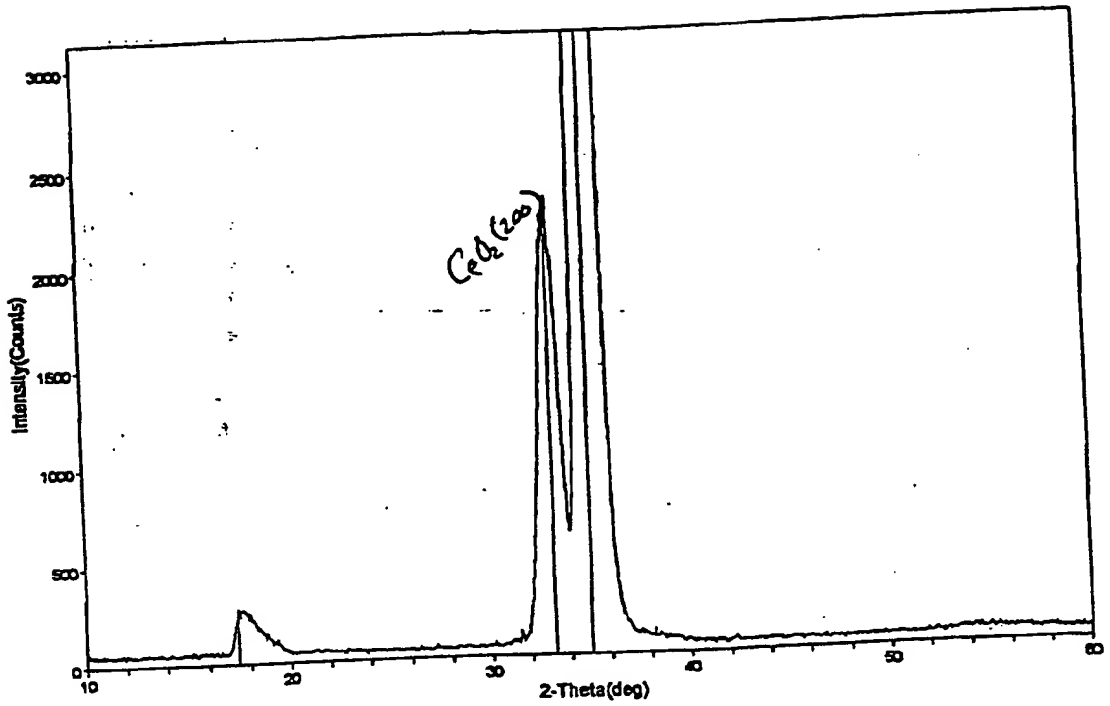
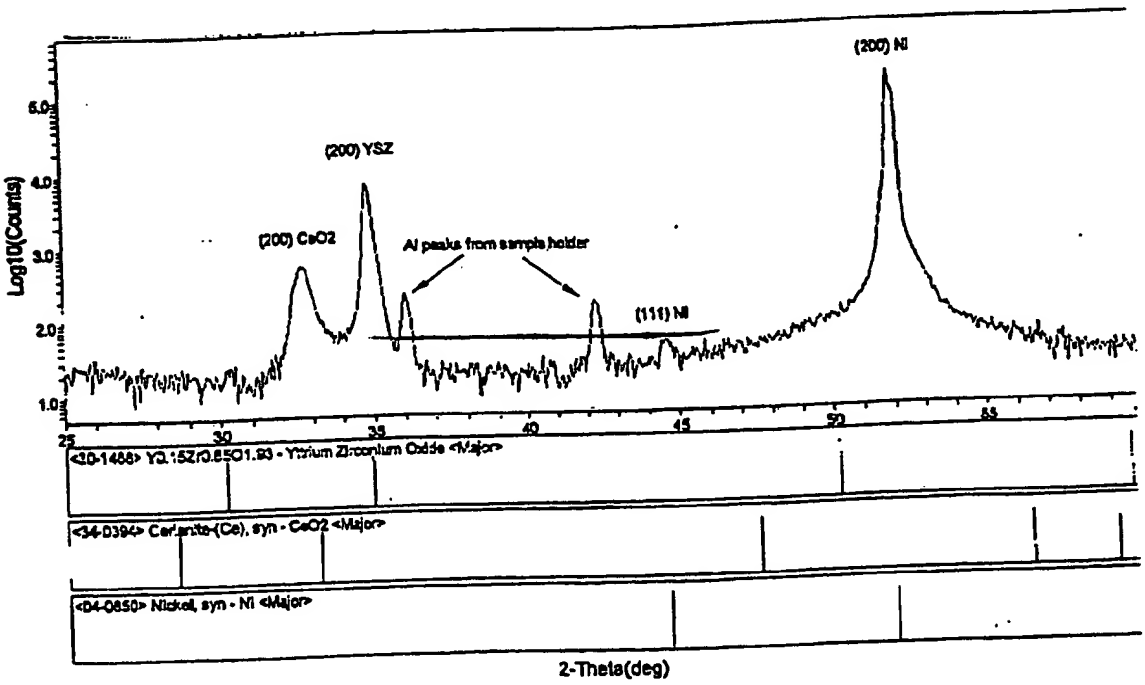

CeO2(200)
Intensity(Counts)
2-Theta(deg)

Fig. 13


(200) Ni
(200) YSZ
(200) CeO2
Al peaks from sample holder
(111) Ni
Log10(Counts)
<30-1468> Yttrium Zirconium Oxide <Major>
<34-0394> Cerianite-(Ce), syn - CeO2 <Major>
<04-0850> Nickel, syn - Ni <Major>
2-Theta(deg)